QUARTERLY PROGRESS REPORT

PHASE 3: CLEAN AND SECURE ENERGY FROM COAL

University of Utah
DE-NT0005015
July 31, 2013
Philip J. Smith (PI)
Project Period
April 1, 2013 to June 30, 2013
EXECUTIVE SUMMARY

The University of Utah is pursuing research to utilize the vast energy stored in our domestic coal resources and to do so in a manner that will capture CO₂ from combustion from stationary power generation. The research is organized around the theme of validation and uncertainty quantification through tightly coupled simulation and experimental designs and through the integration of legal, environment, economics and policy issues. The results of the research will be embodied in the computer simulation tools which predict performance with quantified uncertainty; thus transferring the results of the research to practitioners to predict the effect of energy alternatives using these technologies for their specific future application. A summary of highlights from the last quarter follows.

During this quarter the Oxycoal Team worked to complete this task with several subtasks submitting their topical report contribution for internal review. Experiments are wrapping up. Particle shadow velocimetry (PSV) was applied to obtain simultaneous particle velocity, shape and size information in flames of Utah Skyline and Black Thunder (PRB) coals, produced in the oxy-coal combustor (OFC). The investigators also examined particle size distributions for various flue-gas recycle options.

The Gasification Team performed extensive troubleshooting to discover the source of the negative mole fractions that were appearing in Arches simulations coupled with RMCRT (reverse Monte Carlo ray tracing) or DOM (discrete ordinate method) radiation solvers. The problem, which involved erroneous extrapolation for out-of-bounds values, was identified and eradicated. Verification testing was performed on the solutions obtained from the coupling of the new gas properties model with Arches. For the experimental subtasks, the investigators (a) corrected centerline gas temperature profiles for radiation losses from the thermocouple bead at 4 steam gasification conditions in the HPFFB reactor; (b) collected char samples under steam gasification conditions for the Utah Skyline coal char at 10, 12.5, & 15 atm in the HPFFB reactor; and (c) measured particle velocities of Utah Skyline char in the HPFFB reactor with a high-speed camera to calculate particle residence times. They also performed PSV measurements of slurries made from various fuels, and different solids loadings show differences in velocity and droplet size along the centerline and edge of the spray. These differences are primarily a function of gas flow rate and slurry properties. Higher gas flow tends to form smaller droplets overall, with more influence along the centerline of the spray than the edge. Viscosities of these same slurries were measured in a viscometer. It was challenging to acquire consistent data at low shear rates, but at high shear rates shear thinning was generally observed.

During this quarter, the CLC team created simulations to evaluate the sensitivity of HPC simulations for experimental CLC systems with no reactions and to compare our results with data available in literature. Namely, they began to perform cold-flow fluidized validation against experimental data from the literature. Preliminary results in 2-dimensional cases are presented. The kinetics of oxidation of Cu₅O are modeled using two different temperature regimes: low temperature oxidation at temperatures below 700°C using a pore-blocking kinetic model, and a high-temperature regime (above 800°C) using the kinetics of nucleation/growth given by Avrami-Erofeev. It is clear, unlike previous attempts, that the modeling of Cu₅O oxidation does not just involve a firm understanding of the driving force given by a function of the partial pressure of oxygen. On the experimental side, the use of solid fuels in chemical-looping was successful for the two oxygen carriers studied. It is interesting to note that the reaction rate
challenges of this process are not due to slow reactivity of the carrier, but, interestingly, the slow reactivity of the fuels selected and the shallow bed used. The oxygen carriers released the coupled oxygen at rates faster than combustion, which is evidenced by the incomplete combustion of the petcoke and char particles. While these lower reactivity fuels were tested, oxygen was still present in the effluent stream, and before complete combustion the oxygen carriers were completely spent of all CLOU available oxygen.

The UCTT Team performed experiments to evaluate the reproducibility of the coal-pyrolysis scoping studies. For the gas-phase products, the results show reasonable agreement with the original scoping studies, but in most tests the product liquid and gas ratio (liquid/gas) show distinct differences compared to previous experiments. The reason for these differences is still unclear, and more tests need to be performed to provide explanation. Additional isotherms have been completed on some of the thermally treated coals. The data set on the raw coals is now complete as well as the data sets for the Skyline (Utah) coals treated at 0.1 °C/min and the Carlinville (Illinois) coal treated at 10° C/minute. Both of these coals show similar trends. In all cases, the coals treated to 325 °C have a gas capacity less than the fresh coals. Gas capacity increases with treatment temperature. Coals treated with a heating rate of 0.1 °C have a higher gas capacity than coals treated at 10° C/min. Expected trends such as gas content being higher at 50 °C compared to 70 °C and the adsorption of CO₂ being more preferential than methane are also consistent. Since the trends hold over two different types of coals, these trends may extrapolate to other types of thermally treated coals.

Task 9 efforts focused on improving the BSF simulations. Scaling studies of the BSF simulations show that computation efficiency decreases as the processor number increases. The reason that scaling performance is poor is due to the complex flow field and the boundary conditions. Our CPU profiling results shows that PressureSolver is responsible for most of the cost, and they are developing strategies for improving scaling. In addition, the investigators focused on improving the LES calculation efficiency for large-scale parallel simulation cases and improved it by approximately 30%. They also evaluated various radiation models for OFC and determined that RMCRT needs additional study. A series of tests were run on the oxy-coal combustor (OFC) to study the behavior of flames of different types of pulverized coal. We applied the previously developed simultaneous mid-wave infrared and high-speed video technique, along with color video imaging of the flames. Heat flux, temperature, flame velocity and soot concentration profiles along the flame axes were obtained.

RESULTS AND DISCUSSION

Task 1.0 – Project Management

During this quarter, the Project Team submitted the thirteenth quarterly report and continued to work with the Program Manager to ensure that the tasks and subtasks are on target. We also continued to receive contributions to the Phase 3 topical reports and are in the process of reviewing them.

Task 2.0 – Technology Transfer and Outreach

Task 2.0 focuses on outreach and education efforts and the implementation of the External Advisory Board (EAB) recommendations. After extended discussion this quarter, the decision has been made to disband the EAB due to the impending end of federal funding for projects currently overseen by the
Board. It was decided that President David Pershing, acting in his capacity as the Director of the EAB, will communicate the same to EAB members next quarter.

Finally, we completed the deliverable of a minimum of 8 papers related to clean coal utilization for power generation. These include:


**Task 3.0 – Power Generation “Retrofit”: Oxy-Coal**

**Subtask 3.1 – Oxy-Coal Combustion Large Eddy Simulations**

The investigators have submitted several publications on this work to peer-reviewed journals and are working on the requested revisions. In addition, the team completed its contribution to the topical report, and they are posting the information for the final milestone on the project website.

**Subtask 3.2 – Near-Field Aerodynamics of Oxy-Coal Flames with Directed Oxygen and Minimum Flue Gas Recycle**

Work this quarter focused on analyzing results for the topical report.

**Subtask 3.3 – Advanced Diagnostics for Oxy-Coal Combustion**

The PSV method has been discussed in previous quarterly reports. In brief, backlit, high-resolution and high-magnification images of flowing coal particles were acquired and analyzed with an image-processing algorithm.

The studied conditions were similar to those used in the visible-infrared study (see Section 9.3). Only two coal types were studied, Utah Skyline and PRB Black Thunder. Images were acquired at different axial locations in the flame: 5, 20, 35 and 50 cm below the burner. The imaged areas were approximately 25 mm² in size. 6000 double-frame shadowgraphs were acquired for each condition and height.
Figure 1 shows probability distributions of particle size, velocity and shape of Utah Skyline coal particles in two different combustion conditions and four different axial locations in the flame.

No apparent shrinking of the particles was indicated by the particle size distributions over the studied axial distance. Some swelling occurred, indicated by slightly shifted modes in the distributions. The location where the highest mode occurred was affected by the oxygen concentration in the primary stream: the largest particles were detected around 20 cm below the burner in the 20% O₂ concentration case, while with 0% O₂, this location shifted to around 35 cm. In each case, after the swelling, particles began to shrink, indicating burnout and fractioning, but within the imaged portion of the flame axis, they did not shrink below their original sizes.

Particle velocities showed the same trend in both cases shown: velocities started at around 6 m/s and increased slightly up to a maximum, from which they decreased to 4 m/s on average, as the axial coordinate increased.

There were no identifiable differences in the particle shape distributions. This means that the coal particles retained their initial shapes regardless of oxygen concentration and axial position. There were no identifiable elongated particles present in the flames, which we found in smaller scale flames. At this point, we hypothesize that the high shear rates in the turbulent flame disintegrated these elongated char particles before they could form.
Bivariate probability distributions of particle size and velocity indicated that there were no apparent correlation between particle size and velocity, which can be an effect of isotropic turbulence. Bivariate particle size – particle shape statistics indicated a slight correlation between the two in all cases, suggesting that less spherical particles traveled slower, on average, than more spherical ones.

When analyzing the images it was found that many of the acquired images showed inadequate contrast. Apart from blurring caused by being off-focus, beam steering in the high temperature turbulent flow was identified as a possible cause of this. With the current equipment, this beam steering cannot be avoided, however, with image deconvolution, its effects can be reduced. A deconvolution module for the already developed image processing framework is being developed.

The remaining image sets are being processed.

**Subtask 3.4 – Oxy-Coal Combustion in Circulating Fluidized Beds**

This subtask has been discontinued, and the investigators are summarizing their work for a topical report.

**Subtask 3.5 – Single-Particle Oxy-CO₂ Combustion**

**Single-particle CFB**

Efforts this quarter continued to focus on data analysis in preparation for drafting this contribution for the topical report.

**Single-particle char oxidation**

The investigators submitted their topical report this quarter and are addressing comments.

**Subtask 3.6 – Ash Partitioning Mechanisms for Oxy-Coal Combustion with Varied Amounts of Flue Gas Recycle**

**Ash partitioning mechanisms in lab-scale oxy-coal combustion**

This portion of the subtask is complete.

**Ash partitioning mechanisms in pilot-scale oxy-coal combustion**

**Coal properties and combustion conditions.** As described in previous quarterly reports, Powder River Basin coal (PRB, sub-bituminous) is used for ash aerosol formation mechanisms research under oxy-coal combustion with different recycle options and amounts. PRB coal contains high moisture (23.69 wt %), low ash and low sulfur. Its proximate analysis, ultimate analysis and ash composition data are shown Table 1 and Table 2.

<table>
<thead>
<tr>
<th>Ash (%)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>S (%)</th>
<th>O (diff) (%)</th>
<th>LOD</th>
<th>V (%)</th>
<th>FC (%)</th>
<th>HHV(BTU/lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.94</td>
<td>53.72</td>
<td>6.22</td>
<td>0.78</td>
<td>0.23</td>
<td>34.11</td>
<td>23.69</td>
<td>33.36</td>
<td>38.01</td>
<td>9078</td>
</tr>
</tbody>
</table>
As described previously, cases of oxy-coal combustion with three different recycle cleanup options and two recycle amounts were conducted on Oxy-Fuel Combustor (OFC). CO₂ concentrations in all these cases are between 88% - 95%, with 2% - 4% O₂ in the dry basis. Both primary and secondary streams were recycled CO₂, no pure CO₂ was used in these cases.

Four different recycle cleanup options are: 1) RFG with ash removed, which means recycle flue gas after baghouse; 2) RFG with ash and moisture removed, which means recycle flue gas after condenser; 3) RFG with ash, moisture and sulfur removed, which means recycle flue gas after scrubber; 4) FGR with nothing removed, which means recycle totally dirty flue gas, this case is not finished yet. And two recycle amounts are: 1) 27% inlet O₂ oxy-coal combustion; 2) 50% inlet O₂ oxy-coal combustion. Cases with case description as well as status are shown Table 3. Currently, we have finished the ash aerosol sampling with BLPI for all the cases except the FGR with nothing removed.

Table 3. Combustion cases.

<table>
<thead>
<tr>
<th>Cases</th>
<th>Description</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIR</td>
<td>air combustion</td>
<td>done</td>
</tr>
<tr>
<td>OXY50 Once</td>
<td>oxy-coal combustion with 50% inlet O₂ and once through CO₂</td>
<td>done</td>
</tr>
<tr>
<td>OXY50 RFG Ash</td>
<td>oxy-coal combustion with 50% inlet O₂ and RFG after baghouse</td>
<td>done</td>
</tr>
<tr>
<td>OXY27 RFG Ash</td>
<td>oxy-coal combustion with 27% inlet O₂ and RFG after baghouse</td>
<td>done</td>
</tr>
<tr>
<td>OXY50 RFG Ash-H2O</td>
<td>oxy-coal combustion with 50% inlet O₂ and RFG after condenser</td>
<td>done</td>
</tr>
<tr>
<td>OXY27 RFG Ash-H2O</td>
<td>oxy-coal combustion with 27% inlet O₂ and RFG after condenser</td>
<td>done</td>
</tr>
<tr>
<td>OXY50 RFG Ash-H2O-S</td>
<td>oxy-coal combustion with 50% inlet O₂ and RFG after scrubber (fully clean)</td>
<td>done</td>
</tr>
<tr>
<td>OXY27 RFG Ash-H2O-S</td>
<td>oxy-coal combustion with 27% inlet O₂ and RFG after scrubber (fully clean)</td>
<td>done</td>
</tr>
<tr>
<td>OXY50 RFG Dirty</td>
<td>oxy-coal combustion with 50% inlet O₂ and dirty RFG</td>
<td>to be</td>
</tr>
<tr>
<td>OXY27 RFG Dirty</td>
<td>oxy-coal combustion with 27% inlet O₂ and dirty RFG</td>
<td>to be</td>
</tr>
</tbody>
</table>

**Results.** The ash aerosol particle size distribution (PSD) for cases of three different recycle cleanup options and two different recycle amounts are shown in Figure 1. Figure 1 (a) is volume based PSD which means aerosol mass of per unit volume (µg/m³) versus particle size (µm), it contains the information of ash aerosol concentration characteristics; Figure 1 (b) is input ash based PSD showing aerosol mass per unit input ash (µg/g) versus particle size (µm), and it contains the information about aerosol formation mechanisms.

Figure 1 shows that the ash aerosol PSDs have two modes in all recycle conditions, which suggests different recycle cleanup options and amounts may not affect the ash aerosol formation mechanisms. However, the nucleation mode shifts from 0.06µm to 0.17µm when switching from 27% inlet O₂ cases to 50% inlet O₂ cases, while the coarse mode remains the same. This might be caused by the higher combustion temperature in 50% inlet O₂ cases, since higher combustion temperature will enhance the vaporization of the minerals, subsequently increasing the concentration of nucleation mode particles (0.06µm). Therefore, the coagulation rate of the nucleation mode particles will be largely increased.
because the coagulation rate is proportional to the square of the particle number concentration, and this process could help shift the nucleation mode to a larger size (0.17µm). Meanwhile, Figure 1 shows a higher ash aerosol concentration in 50% inlet O₂ cases. For the volume based concentration, Figure 1 (a), ash aerosol concentrations in 50% inlet O₂ cases are higher in all particle size ranges, which is most probably caused by the reduction of the total flue gas flow rate from 23.59 Nm³/h in 27% inlet O₂ cases to 13.36 Nm³/h in 50% inlet O₂ cases. For the input ash based concentration, as shown in Figure 1 (b), ash aerosol concentrations in 50% inlet O₂ cases are higher only in the particle size range of 0.06µm to 0.54µm, due to higher combustion temperature in 50% inlet O₂ cases.

Different recycle cleanup options do not seem to affect the PSD significantly. However, it might affect the ash aerosol compositions, and this research is underway.

Figure 2. Aerosol particle size distribution: (a) volume based; (b) input ash based.

**Task 4.0 - Power Generation “Retrofit”: Gasification**

Subtask 4.1 – Entrained-Flow Gasifier Simulation and Modeling

This subtask has been discontinued, and the investigators are summarizing their work for the topical report.

Subtask 4.2 – Subgrid-Scale Mixing and Reaction Modeling

During this quarter, the investigators completed a revised draft of their contribution to the topical report.

Subtask 4.3 – Radiation Modeling

Close inspection of the Arches heat loss model revealed that in rare cases, some of the computational cells contained heat loss values that exceeded the table threshold value. In these instances, the heat loss table extrapolated along the trend line and returned values that may be unphysical, such as negative mass fractions. The problem was eradicated by implementing a clipping mechanism that prevents the algorithm from extrapolating beyond its pre-computed limits.
Once the simulations were no longer producing negative mole fractions, further verification testing was carried out to ensure that the coupling between the new radiation properties model and Arches was implemented correctly. The verification testing included implementing a manufactured solution wherein the gas absorption coefficient was assigned the value of the sum of the mole fractions of the five radiatively participating species. The absorption coefficients that were generated by the property calculator were compared with an independent script that converted the mixture fractions to mass fractions, and then to mole fractions, which were summed as explained above. Identical results from the property calculator and independent script confirmed the verification for this test.

With the problem eradicated, the gas-phase absorption coefficients could be modified to include the effect of the coal-particle absorption coefficients. An oxy-coal furnace simulation was selected as a demonstration case for the new capability. Results are shown in Figure 3.

Figure 3. Temperature field of a center-slice of an oxy-coal furnace simulation. The radiative heat transfer is calculated with a RMCRT model that incorporates entrained coal particles.

Subtask 4.4 – Char and Soot Kinetics and Mechanisms

Gas Temperature Profiles Corrected for Radiation. Centerline gas temperature profiles were measured at 4 gas conditions in the high-pressure, flat-flame burner (HPFFB) reactor using a B-type thermocouple.
The diameter of the thermocouple bead was 422 µm. The gas temperature was solved using an energy balance of the thermocouple bead. The bead is heated by convection and is cooled by radiating heat away to the cooler reactor walls. Conduction through the thin, relatively long wires coming off from the thermocouple bead is ignored. Assuming that the thermocouple bead is at equilibrium, the following energy balance is used:

\[ Q_{\text{convection}} = Q_{\text{radiation}} \]  
\[ (4.4.1) \]

\[ h \cdot A_{\text{bead}} \cdot (T_{\text{gas}} - T_{\text{bead}}) = A_{\text{bead}} \cdot \sigma \cdot \varepsilon \cdot (T_{\text{bead}}^4 - T_{\text{wall}}^4) \]  
\[ (4.4.2) \]

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

\[ \varepsilon = -0.1 + 3.24 \times 10^{-4}T - 1.25 \times 10^{-7}T^2 + 2.18 \times 10^{-11}T^3 \]  
\[ (4.4.3) \]

where \( T \) is the bead temperature in Kelvin. The emissivity expression in Equation 4.4.3 predicts a value of 0.12 at 1000 K and 0.22 at 2000 K. The temperature correction is very sensitive to the emissivity value of the thermocouple bead, but using the expression in Equation 4.4.3 led to temperature corrections around 100 K at gas temperatures near 1800 K.

The centerline gas temperature profiles for the 4 steam conditions of the HPFFB reactor are summarized in Figure 4 and have been corrected for radiation losses from the thermocouple bead as discussed above. The different conditions are identified by the total pressure and the peak gas temperature measured from the profile. For example, the 15 atm 1830 K temperature profile was measured at 15 atm total pressure and had a maximum measured centerline gas temperature of 1830 K. Only 3 inches of the 15 atm 1611 K temperature profile is shown in Figure 4 since 3” is the greatest reaction length (i.e., distance between burner and collection probe) used at this condition.
Steam Gasification Experiments. The majority of this quarter was spent collecting chars in the HPFFB under steam gasification conditions for the Utah Skyline char at total pressures of 10, 12.5, and 15 atm. Similarly as was done in the previous quarter using Illinois #6 chars, the Utah Skyline gasification experiments were conducted using a re-injection approach where fully pyrolyzed coal chars were fed in the HPFFB reactor at steam conditions. The coal chars were pyrolyzed in the HPFFB reactor at the same total pressure that they later would be re-injected. In contrast to the Illinois #6 gasification experiments where the 75-106 µm fraction was re-injected at steam conditions, the Utah Skyline steam gasification experiments utilized the 45-75 µm fraction. The size fraction of coal char used during gasification re-injection experiments was determined solely by which size fraction contained the highest yields during the production of pyrolyzed chars. Since 45-75 µm raw coal was fed during the generation of both Illinois #6 and Utah Skyline pyrolyzed chars, char swelling during pyrolysis had a greater effect on Illinois #6 than the Utah Skyline coal.

The data set involving the steam char gasification of Utah Skyline chars is now complete. The mass release data of the Utah Skyline char from HPFFB experiments at steam gasification conditions are shown on a dry ash-free (daf) char basis in Figure 5. Expected trends of increased mass loss with increasing residence time and steam partial pressure are observed. The mass release data in Figure 5 are currently shown at different collection heights above the burner since particle residence times have not yet been calculated. The collection heights summarized in this figure correspond to estimated particle residence times of 60 to 350 ms based on previous calculations of residence times in the HPFFB reactor.
Figure 5. Mass release (daf) on a char basis for steam gasification experiments of Utah Skyline char (45-75 µm) in the HPPFB reactor at total pressures of 10, 12.5, and 15 atm.

All the Utah Skyline steam gasification HPFFB data (at 10, 12.5, & 15 atm) will be used to regress kinetic constants in the near future for a first-order model and for the Char Conversion Kinetics (CCK) model (Shurtz, 2011). These data include mass release values of the Utah Skyline char collected at 4 different gas conditions and 2-3 residence times per gas condition. The post-flame gas environments of the aforementioned gas conditions contain steam at concentrations of 7.4 to 8.6 mol% as predicted by thermodynamic equilibrium at total pressures of 10 to 15 atm. Previous experience has shown that trying to increase the steam concentration in the post-flame gases much beyond 10 mol% can damage the burner used in the HPFFB reactor.

**Particle Velocity Measurements.** Particle residence times in the HPFFB are needed to create an accurate gasification model. For this purpose, a high-speed camera (Kodak EktaPro) was used to measure 45-75 µm Utah Skyline char particle velocities at 1” above the burner surface at 125 frames per second at the 4 steam conditions in the HPFFB. The measured particle velocities are summarized in Table 4 for both Utah Skyline and Illinois #6 coal chars. The measured particle velocities for the Utah Skyline char were greater than the Illinois #6 char at the 4 steam conditions. The faster particle velocities of the Utah Skyline char are easily explained by the smaller size fraction of char particles used (i.e. 45-75 µm) when compared to the Illinois #6 (75-106 µm). The measured particle velocities will be used in the near future to calculate particle residence times at the four steam gasification conditions for the two coals.

Table 4. Measured particle velocities of Illinois #6 and Utah Skyline coal chars at steam conditions in the HPFFB reactor at 1” above the burner surface.

<table>
<thead>
<tr>
<th>Steam Condition</th>
<th>Illinois #6 char (75-106 µm)</th>
<th>Utah Skyline char (45-75 µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V_p (m/s)</td>
<td>V_p (m/s)</td>
</tr>
<tr>
<td>10 atm 1814 K</td>
<td>0.758</td>
<td>0.828</td>
</tr>
<tr>
<td>12.5 atm 1782 K</td>
<td>0.641</td>
<td>0.741</td>
</tr>
<tr>
<td>15 atm 1611 K</td>
<td>0.572</td>
<td>0.634</td>
</tr>
<tr>
<td>15 atm 1830 K</td>
<td>0.663</td>
<td>0.716</td>
</tr>
</tbody>
</table>
Subtask 4.5 – Slag Formation and Slag-Wall Interactions

This subtask is complete.

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

Subtask 4.6a: Characterization of Injector Spray Behavior

This quarter slurry sprays were evaluated by a number of methods, including PSV and patternation. Five slurries were evaluated and compared to pure water. Properties of the slurries are shown in Table 5. A micro-hole injector with eight 0.023 inch holes was used in this analysis.

Table 5. Description of the liquids evaluated.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Solid</th>
<th>Liquid</th>
<th>Solid (wt%)</th>
<th>Mass average particle size (micron)</th>
<th>Viscosity @ 50 s⁻¹ (Pa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>---</td>
<td>Water</td>
<td>0</td>
<td>n/a</td>
<td>0.000888</td>
</tr>
<tr>
<td>Slurry A</td>
<td>Coal</td>
<td>Water</td>
<td>31</td>
<td>69.1</td>
<td>0.00579</td>
</tr>
<tr>
<td>Slurry B</td>
<td>Coal</td>
<td>Water</td>
<td>53</td>
<td>69.1</td>
<td>0.374</td>
</tr>
<tr>
<td>Slurry C</td>
<td>Coal</td>
<td>Water</td>
<td>57</td>
<td>69.1</td>
<td>1.03</td>
</tr>
<tr>
<td>Slurry D</td>
<td>Petcoke</td>
<td>Water</td>
<td>37</td>
<td>77.1</td>
<td>0.0608</td>
</tr>
<tr>
<td>Slurry E</td>
<td>Petcoke</td>
<td>Water</td>
<td>43</td>
<td>77.1</td>
<td>0.125</td>
</tr>
</tbody>
</table>

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

Imaging was focused on two positions. One position was along the center axis of the spray, centered two inches below the bottom face of the atomizer, which can be traced from the slurry tubing direction. The other portion of the spray was along the edge, also 2 inches below the bottom face of the atomizer. The edge position was roughly 2 inches to the side of the spray’s center axis. Figure 6 shows images of the camera and injector alignment.
Figure 6. PSV equipment and injector alignment.

Three levels of airflow and two levels of liquid flow were explored. Figure 7 shows the average drop size along the center axis of the spray for various slurry loadings of both coal and pet coke. Figure 8 shows the average drop size along the edge of the spray.

Figure 7. Effect of gas and liquid flow on the average drop diameter along the spray’s center axis.
In general, increased gas flow tends to decrease the drop diameter in the center of the spray. There were three instances where this was not the case. For the coal slurries, both liquid flow rates of the 31 wt% slurry and the 12 gph case for the 57 wt% slurry show slight increases in the average drop diameter as the airflow is increased. For the petcoke slurries, both liquid flow rates of the 37 wt% slurry show slight increases in the average drop diameter as the airflow is increased. Standard deviations are still being calculated for each case over the many images captured. The standard deviations might show that those increases in diameter with airflow are within the standard measurement error. It seems the lower loadings of both fuels show this behavior, yet the water cases do not. Both water cases show a decrease in the average drop diameter as the airflow is increased. Additionally, both 43 wt% petcoke slurries and the 10 gph 57 wt% coal slurry show a decrease in average drop diameter with an increase in airflow.

A possible explanation for the slight increases in average drop diameter with airflow for the lower slurry loadings could be tied to the physical properties of the slurries and the atomizer geometry. The atomizer has an inner bevel, which sometimes allows the atomized liquid to adhere to the atomizer’s face. This is seen more for slurries than for water, both because the slurry is more visible and likely because the slurry can dry out leaving a solid fuel residue. The higher slurry loading may be viscous enough that as they exit the atomizer, they are thick enough to only be propelled down by the atomizing air. The lower slurry loadings may adhere enough to the atomizer’s bottom face to form drops, which as the airflow increases, are more prone becoming entrained with the airflow. These drops would cause the average drop diameter to increase as they are not subject to the same magnitude of atomizing air as the slurry not adhering to the atomizer’s bottom face. Future tests involving short videos of the actually atomizer could elucidate the degree to which each liquid adheres to the atomizer’s face.

For almost every case along the center of the spray, as the liquid flow rate is increased, the average drop diameter increased. The only case where this does not happen is for the 57 wt% coal slurry and an airflow
of ~1.4 lb/hr. In this case, the difference between the average diameters is ~3 micron, which is likely within the standard error of the measurements.

At the edge of the spray, the relation between airflow and drop diameter is less predictable. Most of the cases in Figure 8 showed a slight reduction in drop diameter with an increase in airflow. The exceptions are both liquid flows of the 43 wt% petcoke slurry, the 10 gph flow of the 53 wt% coal slurry, the 12 gph 37 wt% petcoke slurry, and the 12 gph water case. The 12 gph 37 wt% petcoke slurry is the only one of these that increases in average diameter with every increase in airflow, and the increase is ~6 micron, which is likely within the margin of error of the measurement technique. The other cases listed show either an increase followed by a decrease in average drop diameter with increasing airflow, or vice versa. It could be that this is a result of liquid adhering to the bottom face of the atomizer. In the 43 wt% petcoke slurry case, the initial increase in average drop diameter could be explained by an increase in the entrainment of these drop forming on the edge of the atomizer’s bottom face. The then subsequent decrease in average drop diameter with increasing airflow could be explained by better atomization of those entrained drops. In the 53 wt% coal slurry case, a similar explanation could be offered, except the steps are shifted by the increased slurry viscosity. Again, in order to identify this as the mechanism at work, short videos of the atomizer’s bottom face should be obtained.

Figure 9 shows the average spray direction along the center of the spray. Figure 10 shows the average spray direction along the edge of the spray. In Figure 9 and Figure 10, 270° is straight down along the center axis of the injector. 0° is horizontal to the left.

![Figure 9. Effect of gas and liquid flow on the average spray direction along the center of the spray.](image-url)
Figure 10. Effect of gas and liquid flow on the average spray direction along the edge of the spray.

The spray direction is measured in degrees, where when looking directly at the spray, 0° is the negative horizontal axis, 90° is the positive vertical axis, 180° is the positive horizontal axis, and 270° is the negative vertical axis. The injector’s center axis points along the 270° line, so for a 270° spray direction, the spray is moving straight down. For comparison, 0° corresponds to a line from the center to the right of any of the subplots in Figure 11, as well as to the left in the images shown in Figure 6. There is little variation in the direction of the spray in the center of the spray. As shown in Figure 9, increasing the airflow serves to move the spray direction closer to 270° degrees, regardless of liquid flow rate, fuel type, or fuel loading.

At the edge of the spray, the spray direction is more erratic, as shown in Figure 10. As the left edge of the spray was imaged, it would be expected that if a trend in direction exists, it would be to the left, or towards 0°/360°. For almost all cases, increasing the airflow results in either no significant change in the average spray direction, or the average spray direction moves more to the left, towards 0°/360°. The only case not following this trend is the 10 gph 53 wt% coal slurry. It shows little change in direction for the first airflow increase, and a movement back towards center for the second airflow increase. This could help explain the behavior of the average drop diameter for the same case in Figure 8. Figure 8 shows an increase in the average drop diameter for the second airflow increase. The increased mass of these larger drops are going to require more force to propel them in a direction other than straight down. The increased prevalence of these larger drops likely moves the average spray direction towards 270°. This logic dictates that the same behavior would be seen with the first airflow increase for both liquid flow rates of the 43 wt% petcoke slurry. As the average drop diameter increases with the first airflow increase, it stands to reason that the larger drops would move the average spray direction towards 270°, just as with the 53 wt% coal slurry. The 43 wt% petcoke slurry is less viscous than the 53 wt% coal slurry, and the drops could be more easily atomized leading to no substantial change in the average spray direction. Again, more work is needed to fully determine the dynamics at work.
Patternation tests were performed 16” below the bottom face of the atomizer. A comparison between spray patterns of pure water and a 53% coal slurry are presented in Figure 11. The spatial distribution of water within the spray is rather insensitive to either air or water flow. For a liquid flow of 10 gph, the increase in air flow does seem to increase the fraction of the spray that falls along the spray’s center axis. For a liquid flow of 12 gph, there is almost no change in the spray patternation as the air flow is increased. There is some slight change in the boundary representing the 0.1 fraction of water, but that is small enough to be just slight spray variation.

The 53 wt% coal suspension patternation is more sensitive to both air and liquid flow than the water patternation. As the liquid flow is increased, a more defined center of the spray is seen. For the 10 gph case, increasing the airflow leads to a very poorly defined spray center, which could also be described as a more constant flux along a larger area of the spray’s center. The liquid is much better distributed with the increase in airflow, although little difference is seen between the two highest airflow rates. For the 12 gph case, as the air flow is increased, the position of largest liquid flux is first seen to move, and the liquid becomes better dispersed.

![Figure 11. Effect of air and liquid flow on the patternation of water (left) and a 53 wt% coal slurry (right).](image)

When comparing the direction of the 53 wt% coal slurry in Figure 10 with the patternation results in Figure 11, some agreement is found. For the 12 gph case, as the air flow is increased, the direction of the drops at the edge of the spray tends more towards horizontal. This can be seen as increased area of the 0.3-0.4 fraction in the patternation results. For the 10 gph case with respect to increasing airflow, there is an initial change in direction towards horizontal, before another change back towards the downward direction. In the patternation results with respect to increasing airflow, dispersion initially increases, which could lead to an increase in flow in the horizontal direction. Then, oscillation is seen in the dispersion area, which could lead to a change in flow towards the downward direction. These effects are not exactly clear, but some relation can be seen.
Rheology. Fuel suspensions often have unique rheological properties, as the solid loading of the suspensions is often maximized so as to increase the energy density. These highly loaded suspensions exhibit shear-dependent behavior. Atomization quality has been shown to be inversely proportional to the viscosity of the suspension (Ahmed and Hasan 1993). Suspension viscosity has been shown to be a function of solid concentration, solid average particle size, and the physiochemical properties associated with the fuel (Roh et al. 1995; Hasan, Baria, and Rao 1986; Son and Kihm 1998). Typically, decreasing the average particle size leads to an increase in viscosity, and an increase in solid loading increases the viscosity. Roh et al. (1995) suggests that the more hydrophobic a fuel particle is, the lower the viscosity will be for comparably high solids loadings. Fuel suspensions have been shown to have a minimum viscosity at maximum solids loading if the particle size distribution is set to provide the maximum bulk density (Ateşok et al. 2002).

The viscosities of the slurries shown in Table 5 were measured in a viscometer. The results of these experiments are shown in Figure 12. All suspensions exhibited non-Newtonian behavior. The petcoke suspensions seemed to be shear thinning, while all coal suspensions seemed to be shear thickening with the exception of the 57 wt% coal suspension in water.

![Figure 12. Viscosity of multiple coal or petcoke slurries as a function of shear rate.](image)

Both the 37 wt% and the 43 wt% petcoke suspension are clearly shear thinning, as shown in Figure 12. The 31 wt% coal slurry and the 53 wt% coal slurry are both shear thickening, although the data for the 53 wt% coal suspension doesn’t as clearly indicate this behavior. Above ~50 inverse seconds, the data converges quite nicely. However, below ~50 inverse seconds, the data diverges.

The most uncertainty in the viscosity measurements likely lies at lower values of the shear rate. This uncertainty stems from the increased difficulty in acquiring reproducible data. Often times, small shear stresses were initially applied to determine the value needed for the sample to flow. This small shear stress typically corresponded to the lower shear rates. As the shear stress was ramped up and down multiple times for multiple samples of the same suspension, a seemingly representative viscosity was identified. Convergent data was found much more quickly at the higher end of the shear stress ramping.
As discussed previously, the lower end of the shear stress ramping produced divergent results, as seen in the 31 wt% coal data in Figure 12.

The 57 wt% coal suspension in water appears to be slightly shear thinning in Figure 12. However, this could be unrepresentative. Using a parallel-plate viscometer on a suspension is not ideal as it can lead to migration of the suspended particles to the outside portion of the sample, yielding an unrepresentative viscosity. Nevertheless, when comparing all suspensions at a constant shear rate, as the solids loading is increased, the viscosity increases regardless of the type of particle when comparing shear rates above ~20 inverse seconds.

Subtask 4.6b: Development of a Probe for In-Situ Measurements

Work on this portion of the subtask focused on integrating results for the topical report.

Task 5.0 – Chemical Looping Combustion Reactions and Systems

Subtask 5.1 – Process Modeling and Economics

During this quarter the investigators integrated their results, submitted their contribution to the topical report, and continued to work on peer-reviewed publications.

Subtask 5.2 – LES-DQMOM simulation of a pilot-scale fluidized bed

In the past, we have worked on validation and verification of cold-flow fluidized beds simulations. We have continued to develop and improve our CFD and CAD models for multiphase flows description. With these improved capabilities and advanced meshing tools, we can obtain an improved description of fluidized beds systems. In this report we describe the progress with the geometry representation of the system and our advances in the modeling approach. We also present a framework for a sensitivity analysis on the modeling of polydispersity for fluidized beds, which, compared to our previous work, includes effects of various particle sizes in the system.

Geometry description. The fluidized bed system is a 0.895 m inner diameter, 6.1 m tall unit shown in Figure 13. An air sparger inside the bed provides sufficient pressure drop to ensure good air distribution. The system was intended for experiments at 0.3 m/s and 0.6 m/s fluidization velocities. For tests carried out at 0.3 m/s, a 0.76 m-PVC pipe manifold was used. For tests carried out at 0.6 m/s, a 0.102 m-PVC ring sparger shown in Figure 14 was used. The ring has 39, 0.0013 m-nozzles facing downward 30° from the vertical. In this study, only configuration for the 0.6 m/s test was considered. The primary cyclone is a 0.2 m diameter dipleg that returns solids back onto the bed surface via an aerated trickle valve. The secondary cyclone has a 0.152 m-diameter dipleg that returns solids to the bed via a butterfly valve. Neither valve was included in the CAD design for simplicity. Figure 15 shows the CAD geometry created in STAR-CCM+. We have also simplified the geometric representation of the ring sparger - instead of considering the octagonal-like shape in Figure 14, the ring was considered as circular. The new circular shape proposed for the geometry should not significantly influence the fluid dynamic behavior of the solids. However, we did retain detailed geometry and locations for the nozzles in the ring sparger.

Mesh Description. We have used regular hexahedral cells (or cuboids) to build a computational mesh for our CFD calculations. The final cell count was approximately 2,300,000. One of the most challenging
parts of the meshing process was the area corresponding to the nozzles. In order to resolve the very fine geometric features, we had to employ multiple levels of refinement to achieve moderate-quality cells. Figure 16 shows some of the details.
Figure 13. Schematic drawing of the bubbling fluidized bed unit.

Figure 14. Ring sparger for air distribution inside the unit.
Figure 15. Fluidized bed unit created in STAR-CCM+. a) Entire unit. b) Ring sparger side view. c) Ring sparger top view.
Figure 16. Meshed geometry. a) Bottom half. b) Top half. c) Mesh refining around the ring sparger.
Diagnosis. In general, 3-dimensional CFD simulations are very expensive. Computational cost and model complexity increase with number of dimensions and the number of cells in the domain. For that reason, it is always a good practice to diagnose possible problems and develop solutions on coarser meshes or reduced-dimension systems. In this case, we have recreated the fluidized bed as a 2-dimensional system to establish the modeling methodology and set numerical parameters that would otherwise take considerable computational resources for a 3-dimensional system.

Inherently, a 2-dimensional approach reduces the geometric complexity of the system and thus has an effect on output of the simulation, which is no longer physically correct. However, the main objective of this 2-d approach was to test implementation of new modeling methodology. While simplifying the geometry, we did try to maintain as many physical details as possible. For instance, even though we estimated nozzles as simple holes in the sparger wall, we retained the magnitude and direction of the flow coming out the holes as in the real unit. Also, cyclones were removed to keep the cell count low in the 2-dimensional approach. Figure 17 shows the 2-dimensional geometry and mesh.

Sensitivity Analysis. Most industrial multiphase systems share a very important feature that determines their fluid-dynamic behavior: the polydisperse character. Although this has been known since the development of the Kinetic Theory of Granular Flow (Sinclair & Jackson, 1989), (Ding & Gidaspow, 1990), only recently, efforts towards the representation of this polydispersity character through modeling approaches have been carried out (Fan, Marchisio, & Fox, 2004), (Marchisio & Fox, Solutions of
population balance equations using the direct quadrature method of moments, (2005), (Passalacqua & Fox, 2010). In this study, we are performing a sensitivity analysis of the modeling technique for the polydisperse character of the fluidized bed.

Table 6 summarizes the polydispersity sensitivity analysis methodology. Three characteristics are chosen to represent polydispersity: monodispersity, polydispersity through a finite-dispersed method, and polydispersity through Direct Quadrature Method of Moments (DQMOM).

Table 6. Sensitivity analysis methodology.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Variations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polydispersity</td>
<td></td>
</tr>
<tr>
<td>Monodisperse flow</td>
<td>No PSD</td>
</tr>
<tr>
<td>Class method</td>
<td>5, 8, 11 classes</td>
</tr>
<tr>
<td>DQMOM</td>
<td>3, 4 environments</td>
</tr>
</tbody>
</table>

In the monodispersity case, no particle size distribution (PSD) is taken into account and the bed of particles is represented with one characteristic size (a mean diameter). This case is chosen for comparison to the polydisperse case and the experimental data.

In the polydispersity representation with a finite dispersed method, the experimental PSD is divided into different classes or “bins” (as in a histogram), where each bin represents a particular diameter. In the simulation setup each class is considered as a different phase. The finite-dispersed method considers 5, 8 and 11 bins for this study.

DQMOM was originally developed based on the moment approximation to the population balance equations (PBE), which is the most physically correct set of equations to describe polydispersity in multiphase systems. However, due to the high dimensionality of the PBE description, it is very difficult to couple DQMOM with fluid dynamics simulations. However once coupled, DQMOM methodology can provide a lot of detail for simulations of polydisperse flows. In this study we will test DQMOM with 3 and 4 environments, which correspond to 6 and 8 moment approximation, respectively. The DQMOM technique has been explained in previous developments.

Preliminary Results. As part of the ongoing effort in this sensitivity analysis, we present some of the preliminary results for the monodisperse, 2-dimensional case.
Figure 18. Experimental PSD.

Figure 19. Volume fraction profiles for the monodisperse case at $t = 1.0$ s.
Figure 20. Volume fraction profiles for the monodisperse case at $t = 2.0$ s

Figure 21. Volume fraction profiles for the monodisperse case at $t = 5.0$ s
Based on the experimental PSD (Figure 18) a mean (Sautter) diameter of 104.6 microns was calculated, and bed of particles of the same diameter was set up to simulate the monodisperse case. Figure 19, Figure 20 and Figure 21 show the volume fraction profiles calculated at 1, 2 and 5 seconds into the simulation. The most important characteristic in these profiles is the clear interface between air and solids formed in the bed. The clear separation is characteristic only of monodisperse systems. Comparison of the pressure drop along the axial direction was also performed against experimental data. This comparison is shown in Figure 22.

![Pressure drop monodisperse case. Black dots correspond to experimental data, the orange line correspond to simulation results.](image)

Although this monodisperse simulation is able to reproduce the general pattern of the experimental pressure drop in the axial direction, we can clearly see the sharp separation at the interface depicted by the simulated pressure drop (orange line) at 1 m. The experimental data reveals that a smoother separation happens at 1.5 m, due to the continuous distribution of particle sizes from top (small particles) to bottom (bigger particles) of the bed.

Next, we set up a simulation including polydispersity. We used the Sautter diameter and the variance of the experimental PSD with a polydispersity model implemented in STAR-CCM+. This model tracks the evolution of the mean and the variance of a distribution, with the assumption that it is a lognormal distribution. Clearly, the PSD does not fit lognormal distribution, but the simulation helps to illustrate the effect of polydispersity in the fluidized bed in a simplified way, compared to the other proposed techniques.
Figure 23. Volume fraction profiles for the polydisperse case at $t = 1.0$ s.

Figure 24. Volume fraction profiles for the polydisperse case at $t = 2.0$ s.
Figure 23, Figure 24 and Figure 25 show the volume fraction profiles at 1, 2 and 5 seconds into simulation. It is clear from these profiles that a continuous distribution of particles is forming over the bed and the sharp division between interfaces will be lost as time passes; this feature is not shown in the monodisperse case.

Figure 26. Pressure drop polydisperse case. Black dots correspond to experimental data, the orange line correspond to simulation results.
Contrary to monodisperse case, Figure 26 shows a smoother separation from the bed of solids and improves the description of the axial pressure drop trend.

As previously mentioned, these are preliminary results, which we are using to evaluate our solution methodology and also, which help us to understand behavior of CLC systems in a simplified environment. A full sensitivity analysis is planned to be completed by August 2013.

**Subtask 5.3 – Laboratory-Scale CLC Studies**

**Oxidation of cuprous oxide (Cu₂O)**

Modeling the oxidation of Cu₂O to CuO (Cu₂O + ½ O₂ → 2 CuO) has proven challenging when trying to take into consideration all factors that influence the rate. For the general case a kinetic expression may be represented by a function of individual influences; each playing a role in the overall kinetic rate. This general case may be written as shown in the equation below. The expressions \( f(T) \), \( f(X) \) and \( f(p_{O_2}) \) represent the influences of temperature, conversion and the partial pressure of oxygen, respectively, on the oxidation reaction of Cu₂O.

\[
rate = f(T)f(X)f(p_{O_2})
\]

**Influence of oxygen partial pressure.** It may be possible, by experimental observation, to obtain a kinetic expression, which adequately predicts the rates and/or conversion profiles of a range of copper-based oxygen carriers. For the design of these experiments it is important to first understand \( f(p_{O_2}) \). The understanding of this influence allows for the design of experiments necessary to identify the roles the other two influences play in the kinetic expression.

Figure 27 represents the conversion profiles obtained during the oxidation of Cu₂O on the 45_ZrO2_FG material at 825°C and various oxygen partial pressures. This set of experiments was used to determine the influence the partial pressure of oxygen has on the reaction kinetics of Cu₂O oxidation. If it is assumed that the function, \( f(p_{O_2}) \), takes the following form (common among reversible reactions):

\[
f(p_{O_2}) = (p_{O_2}^{eq} - p_{O_2}^{eq})
\]

then the result obtained from analysis of data used in Figure 27 yields \( \alpha = 1.3 \). That exponent is used in subsequent analysis of oxidation rates.
Influence of degree of conversion \( f(\chi) \). For the oxidation of \( \text{Cu}_2\text{O} \) to \( \text{CuO} \) the conversion versus time profile is given in Figure 28. It has been determined that, especially at the lower temperatures, the data do not express well as any simple zero, first or second order function.

Zhu et al. (2004) suggested that at low temperatures the oxidation of cuprous oxide followed a logarithmic rate law and the resulting activation energy was 38 kJ/mol, which compares very well with the value reported here obtained using the constant driving force approach. These authors suggested that while the logarithmic rate law held true at low temperatures (up to 800°C), the apparent activation energy became very small or negative at higher temperatures. As has been reported earlier, this decrease in rate
at high temperature is due to a decrease in oxidation driving force associated with lower equilibrium partial pressure of oxygen. During their discussion several theories for the logarithmic characteristics of the oxidation rate at low temperature were dismissed including (1) electric fields developed across oxide layers, (2) the tunneling of electrons, (3) and the possible nucleation and growth processes. They were able to describe the mechanism responsible for the apparent logarithmic nature of the reaction rate as a pore-blocking mechanism resulting from the 5% volume increase from Cu$_2$O to CuO. They recommended the use of the model described by Davies et al. as follows:

\[ m = k_1 \ln(k_2 t + k_3) \]

where \( m \) represents the reacting species and \( k_1, k_2 \) and \( k_3 \) represent fitting constants which may be thought of physically as relating to the number of open low-resistance pathways (e.g., pores, grain boundaries, cracks).

Evans (1960) developed a more easily understandable expression along these same lines. In the case of mutually blocking pores (blocking of neighboring pores through compression) the expression is given below and shows that conversion is a function of a blocking constant, \( \lambda \), and a second constant, \( k_d \).

\[ X = \lambda \ln \left( 1 + \frac{k_d t}{\lambda} \right) \]

Utilizing this method several groups were able to show that the effect of pore blocking is commonly a function of temperature. Won and Sohn (1985) successfully accounted for the effect of pore-blocking, as did Sohn and Kim (2002) and Sohn et al. (2004) for very different types of materials. These groups were able to show that the pore-blocking influence may be readily recognized by two separate regimes of reaction rates: the first regime is characterized by quick initial rates and is followed quickly by the second as the reaction rate slows well before full conversion. This phenomenon may be seen in Figure 27 for the case of cuprous oxide oxidation.

It is important to note that while this effect is readily observed for the lower temperature regime, the effect is less obvious at temperatures above 700°C. Therefore another model must be employed for the characterization of the reaction kinetics at higher temperatures.

The low temperature activation energy may be determined when this pore-blocking effect is taken into account. By rearranging equation the previous and plotting the left-hand side, \( \exp(x/\lambda) \), against time the blocking constant is resolved by finding the value that gives the “best-fit” straight line using regression analysis at each temperature. Figure 29 displays the results of the pore-blocking analysis. The pore-blocking constant varies from 0.226 at 600°C to 0.182 at 700°C.
While the pore-blocking model adequately describes the observed kinetic behavior for the low-temperature oxidation of Cu$_2$O, it, however, does not hold well above 700°C. This may be seen in Figure 28. While below 700°C the oxidation rates clearly change long before full conversion, the higher temperature rates actually approach close to full conversion before the effects of pore-blocking may be seen. This is especially true above 800°C.

For the case of high-temperature conversion of Cu$_2$O the nucleation/growth model by Avrami (1939) is used. While this model is generally used for the modeling of the start of reactions it may also be extended to reactions where the individual grain boundaries are small enough that nucleation must occur individually for each grain. Commonly, for metals and powders, Avrami expression is used to model the redox characteristics (Lin 2003; Prisedsky 2004). The expression is given by:

$$[-\ln(1 - X)]^{1/n} = k_{app}t$$

where $n$ represents a constant used to describe the type of nucleation and growth that is occurring. By rearranging:

$$ln[-\ln(1 - X)] = n \ln(k_{app}) + n \ln(t)$$

The growth constant $n$ was determined by a best-fit approach, plotting $ln[-\ln(1 - X)]$ against $n\ln(t)$ and for both carriers it was determined that $n=1$ is matches the experimental data best.

In summary, two sets of models have been used to characterize the oxidation characteristics of Cu$_2$O in oxygen carriers. The first of these, pore-blocking kinetics, has been used to model the kinetic observations of Cu$_2$O at and below 700°C, while the second model, Avrami-Erofeev, has been used to model the oxidation of Cu$_2$O above 800°C. The influence of the solid on the reaction has been identified in each of these cases and is shown in Table 7.
Table 7. Influence of temperature within the two different temperature regimes for the oxidation of Cu$_2$O within two different oxygen carriers.

<table>
<thead>
<tr>
<th>Carrier Material</th>
<th>High Temperature</th>
<th>Low Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>f(X)</td>
<td>N</td>
</tr>
<tr>
<td>45_ZrO2_FG</td>
<td>1-X</td>
<td>n = 1</td>
</tr>
<tr>
<td>50_TiO2_MM</td>
<td>1-X</td>
<td>n = 1</td>
</tr>
</tbody>
</table>

### Influence of temperature on oxidation rate

Using the methods described above the function $f(T)$, or the temperature influence on the reaction, is uncovered by mathematic manipulation. If it is assumed that $f(T)$ takes the form:

$$f(T) = A \times \exp \left( -\frac{E_a}{RT} \right)$$

Then the activation energy and pre-exponential factor are both solved for using the correct models associated with both the high and low temperature regimes. The activation energy calculated for the low-temperature regime is averaged to 168 kJ/mol between both materials and 69 kJ/mol at the higher temperature range. The resulting pre-exponential factors are given as $2.1 \times 10^{12} \text{ (min}^{-1})$ for the lower temperature range and $7.9 \times 10^4 \text{ (min}^{-1})$ at the higher temperature range.

### High Temperature Model Comparison

A summary of experimentally-determined constants for the nucleation/growth kinetic expression is presented in Table 8.

Table 8. Model used to predict the conversion of Cu$_2$O in two different oxygen carriers using the nucleation/growth kinetics expression Avrami-Erofeev.

<table>
<thead>
<tr>
<th>Influence</th>
<th>Model Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f(X)$</td>
<td>$1 - X$</td>
</tr>
<tr>
<td>$p_{O_2,eq}$</td>
<td>$P_{O_2} (\text{atm}) = 6.057 \times 10^{-11} e^{0.02146 T(\degree C)}$</td>
</tr>
<tr>
<td>$f(p_{O_2})$: $(p_{O_2}^{\alpha} - p_{O_2,eq}^{\alpha})$</td>
<td>$\alpha = 1.3$</td>
</tr>
<tr>
<td>$f(T) = A \times \exp \left( -\frac{E_a}{RT} \right)$</td>
<td>$A = 7.90 \times 10^4 \text{ (min}^{-1}); E_a = 69 \text{ (kJ/mole)}$</td>
</tr>
</tbody>
</table>

A comparison of the prediction against the conversion profiles for both materials at 800°C is presented in the left plot of Figure 30. The conversion of the titania material is much faster than the prediction. This may be explained by the change from the low-temperature oxidation mechanism (pore-blocking kinetics) to the high temperature mechanism (nucleation and growth kinetics). There may be some transition period where neither completely accurately describes the true mechanism, but 800°C is irrelevant for the operation of an industrial-scale, chemical-looping reactor. The higher temperatures are more likely to be seen in an industrial/commercial setting (temperatures above 900°C). The right plot of the figure displays the conversion profiles for the titania and zirconia materials along with the predicted values at 925°C. This figure shows the model is better at predicting the higher temperature conversion profiles.
Figure 30. Conversion profiles for the oxidation of Cu₂O at 800°C (left) and 925°C (right) for 45_ZrO₂_FG (□) and 50_TiO₂_MM (Δ), compared against the model prediction (- - -).

Conversion of Solid Fuels with CLOU Carriers

In order to gauge performance of the studied CLOU carriers for converting solid fuels in a fluidized bed, tests were performed in which small batches of fuel were added while the bed was fluidized with nitrogen, allowing oxygen uncoupling. Three different fuels (Illinois #6 coal, Black Thunder coal from the Powder River Basin, and petroleum coke) were used for this study and were converted in the fluidized bed using two different oxygen carriers (50_TiO₂-MM and 45_ZrO₂-MM). The analyses of the tested fuels are provided in Table 9.

Table 9. Analyses of solid fuels used in this study.

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Illinois #6 Bituminous</th>
<th>Black Thunder PRB Sub-bituminous</th>
<th>Green Coke Petroleum Coke</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Proximate Analysis</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture (wt% as received fuel)</td>
<td>2.54</td>
<td>21.30</td>
<td>0.4</td>
</tr>
<tr>
<td>Ash (wt% Dry)</td>
<td>12.33</td>
<td>6.46</td>
<td>0.39</td>
</tr>
<tr>
<td>Volatile matter (wt% dry)</td>
<td>39.40</td>
<td>54.26</td>
<td>11.03</td>
</tr>
<tr>
<td>Fixed carbon (wt% dry)</td>
<td>48.28</td>
<td>39.28</td>
<td>88.01</td>
</tr>
<tr>
<td><strong>Ultimate Analysis (wt% dry ash-free)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>78.91</td>
<td>74.73</td>
<td>89.21</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.50</td>
<td>5.40</td>
<td>3.78</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.38</td>
<td>1.00</td>
<td>1.73</td>
</tr>
<tr>
<td>Sulfur</td>
<td>4.00</td>
<td>0.51</td>
<td>5.82</td>
</tr>
<tr>
<td>Oxygen</td>
<td>10.09</td>
<td>18.27</td>
<td>4.41</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.11</td>
<td>0.08</td>
<td>-</td>
</tr>
<tr>
<td><strong>Heating Value</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HHV, dry (Btu/lb)</td>
<td>12,233</td>
<td>12,815</td>
<td>15,622</td>
</tr>
</tbody>
</table>
The reactivity of the tested fuels, from low to high, is petcoke < Illinois #6 < Black Thunder PRB. Petcoke is stripped of most of the volatile content from the creation process and is less reactive than the coals studied. The Powder River Basin (PRB) coal is a sub-bituminous and thus has a lower rank than the bituminous Illinois #6 coal. The lower rank coals generally have higher reactivities. This ordering may be observed in Figure 31 where the conversion of carbon versus time is displayed for the three fuels during combustion using 50_TiO2_MM material at 930°C. The PRB reacts very quickly reaching full conversion in just a few seconds. The Illinois #6 coal and petcoke, however, do not reach full conversion. From a stoichiometric standpoint, the oxygen supplied by the metal oxide carrier should be more than sufficient to fullycombust all of the fuels. The amount of fuel supplied to the reactor was evaluated by determining the expected amount of oxygen released from the oxygen carrier bed between 20% and 80% conversion from CuO to Cu2O. Therefore, the amount of oxygen released from the carrier should be 40% more than is necessary for complete carbon burnout of the fuel.

![Figure 31: Conversion of three different fuels using 50_TiO2_MM material at 930°C. The conversion is calculated from the mass of carbon (as gas) analyzed and collected by infrared analyzer.](image)

A simple explanation for the lack of full conversion could be that the unreacted fuel was simply blown out of the reactor before it could be consumed. If that is the case the ensuing oxidation cycle would yield no additional carbonaceous products, or at least it would not account for all of the missing carbon. The full conversion profile of the petcoke fuel during the “fuel reactor” cycle with N2 as well as the “air reactor” cycle with air feed is given in Figure 32. Clearly, as the conversion approaches 50% the rate slows considerably and is near zero around 700 seconds of reaction. Air is once again cycled to the reactor around 700 seconds and the missing carbon is burned off. It is clear from this figure that the fuel is not being ejected from the reactor, but is simply not completely reacted within the fluidized bed. The full reaction profile obtained during the combustion of Illinois #6 coal is very similar to the petcoke, in that, it is not fully combusted until the air is once again cycled through the reactor.
Once again, the incomplete combustion of these fuels is not a result of insufficient oxygen supply. Certainly, the fuel is oxygen starved, but it is due to the slow reactivity of the fuel and not due to an excessive charge of fuel to the reactor. This characteristic is accentuated and more easily understood by looking at the effects of increasing the fuel particle size.

The combustion of PRB particles ranging from 150 μm to 6,000 μm (0.3 cm) at 930°C using the 45_ZrO2_FG material is given in Figure 33. The three tests were performed by selecting particles that fit the desired size range while having a very similar combined mass. For example, the sample tested in the 6,000 μm range consisted of only one particle. This single particle had a mass very similar to the combined masses of the other two samples individually. While, once again, the combustion of the small particle size (150 μm) was completed very quickly (roughly one minute) the other two samples did not reach full conversion of the carbon even though the masses of each of the three samples was very nearly equal.

Figure 32: Conversion of carbon during combustion of green petcoke at 930°C using 50_TiO2_MM in a fluidized-bed.
Admittedly, it may be possible to have complete burnout of the larger fuel particles if the amount of oxygen carrier is increased. However, it is likely the case that this will not be due to the increased amount of available oxygen but instead due to an increase in the reaction time due to a deeper particle bed. The slower decomposition rates may be achieved by the oxygen carrier simply due to an increased oxygen partial pressure. The increase in the oxygen partial pressure effectively decreases the driving force for decomposition.

The reactivity of PRB was previously mentioned as being higher than the other two fuels tested. It may be assumed, however, that even for a more reactive fuel there exists a fuel particle size threshold above which a particular oxygen carrier may be ineffective, not because it releases oxygen too slowly, but because it releases oxygen more quickly than it can be consumed by the large particle. The higher rates of oxygen release then produce oxygen that is unreacted and dilutes the fuel reactor product stream. In such a case, “gas polishing” by addition of natural gas to consume the oxygen, may be necessary.

The left plot in Figure 34 shows the conversion of the solid oxygen carrier from CuO to Cu₂O during the combustion of large petcoke particles (roughly 3,000 μm) using 45_ZrO2_FG at 930°C and 960°C. The conversion of the solid oxygen carrier material at 960°C is shown as well. At roughly 200 seconds the oxygen carrier is nearly completely spent and the rate of decomposition slows, essentially to zero. In both cases, the fuel is incompletely combusted and stops reacting as the oxygen is no longer devolved. Due to the increased reactivity of the petcoke at 960°C the conversion profile for that temperature is extended. Once again, while the amount of oxygen is sufficient for the combustion of this fuel, it is simply released and swept away too quickly to react with the remaining petcoke.
Figure 34. Conversion of carbon (left) and oxygen liberation (right) during the combustion of petcoke particles with a diameter of roughly 3,000 μm at two temperatures using the 45_ZrO2_FG material.

The right plot in the figure suggests that the oxygen contained within carbonaceous gas evolved during the combustion of the large petcoke particles accounted for only about 25% of the total evolved oxygen. The remaining 75% of the liberated oxygen was swept through the outlet as unreacted oxygen. This number actually speaks well to the performance of the oxygen carrier, and is undoubtedly a consequence of the relatively shallow bed employed in these tests.

Subtask 5.4 – CLC Kinetics

During this quarter, the investigators are continuing to make revisions to their topical report, based on comments from the internal review process.
Experimental studies

Experiments were performed to evaluate the reproducibility of the scoping studies of core coal pyrolysis experiments and the effects of quartz wool plus stainless mesh (used for holding coal core samples in place, see Figure 35, during the experiments). The following scoping tests (Table 10) revealed some interesting results. For the gas-phase products, the primary species mass shows a reasonable variation, but in most tests the product liquid and gas ratio (liquid/gas) show distinct differences compared to previous experiments. The reason for these differences is still unclear, and more tests need to be performed to provide explanation.

Figure 35. Diagram inside the reactor. A: used in the scoping studies. B: used in the replicates studies.

Table 10. Experimental test matrix for scoping studies.

<table>
<thead>
<tr>
<th>Temperature (C)</th>
<th>Pressure (psi)</th>
<th>Heating rate (C/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>300</td>
<td>10 (3 replicates)</td>
</tr>
<tr>
<td>600</td>
<td>300</td>
<td>1 (1 replicate)</td>
</tr>
<tr>
<td>400</td>
<td>300</td>
<td>1 (1 replicate)</td>
</tr>
</tbody>
</table>

Figure 36 shows the mass distribution of gaseous species for duplicate core coal pyrolysis experiments of 600 C, 10 C/min, 300 psi. As shown from all 4 tests, the methane (CH₄) and CO₂ have a relatively large variation as compared to the other 4 species, but considering that a large coal core sample from a coal block was used instead of a powdered mixture, the variability seems reasonable. Interesting things happened when replicates 2 and 3 were completed. The product liquid to gas ratio (liquid/gas) changed dramatically, from 2.30 to 1.26 (average value), which raises a question: is this due to the difference between the duplicates (i.e., composition variations) or the quartz wool/stainless mesh support?
Quartz wool is a very stable material, and most coal pyrolysis experiments (including high pressure) used this material as packing. As for stainless mesh, it contains a low concentration of nickel (Ni), and may have some catalytic effect on the pyrolysis products (in the high temperature zone), especially with the high pressure H₂ present. Such a process is known as a hydrocracking reaction. In this case, high molecular tars may crack to low molecular tars or gases. In fact the total gas mass increased slightly, while the liquid mass decreased, and thus mass is not conserved unless the lost tar is converted to gases. Another two tests at 1 C/min, 300 psi, 600 C and 400 C showed similar results: small mass changes in the gas phase distribution and a large drop in the liquid/gas ratio (see Figure 37 and Figure 38).

If the Ni in the stainless mesh is not the reason, the inhomogeneity within the coal block used in the experiment might explain the observed variations. Visual inspection of the coal block show clear stratification that could lead to significant differences in cores taken from different regions of the large coal block. More coal analyses need to be performed to evaluate the impact of variability with a coal block.

Figure 36. Mass distribution of gaseous species for duplicate experiments (600 C, 300 psi, 10 C/min).
In the past quarter we continued to develop our HPC simulation tool to simulate underground thermal heating of coal. We have modified geometry introduced in the previous quarterly report, which was created to account for heating of both solid and rubblized pieces of coal and to determine the effect of gaps, or convective channels, on the overall heat transfer inside the coal seam.

In the previous quarter we have introduced rubblized coal bed geometry with three different pipe positions. Because of meshing difficulties associated with those geometries, we have removed the heating pipe from the geometry. Therefore, the new geometry that we are using for our simulations is shown in Figure 39. As previously, the rubblized coal bed interior is 1m x 1m x 1m in size.

Figure 37. Mass distribution of gaseous species in duplicate experiments (600 C, 300 psi, 1 C/min).

Figure 38. Mass distribution of gaseous species in duplicate experiments (400 C, 300 psi, 1 C/min).

**LES in Reacting Porous Media**

In the past quarter we continued to develop our HPC simulation tool to simulate underground thermal heating of coal. We have modified geometry introduced in the previous quarterly report, which was created to account for heating of both solid and rubblized pieces of coal and to determine the effect of gaps, or convective channels, on the overall heat transfer inside the coal seam.

In the previous quarter we have introduced rubblized coal bed geometry with three different pipe positions. Because of meshing difficulties associated with those geometries, we have removed the heating pipe from the geometry. Therefore, the new geometry that we are using for our simulations is shown in Figure 39. As previously, the rubblized coal bed interior is 1m x 1m x 1m in size.
This 1m³ rubblized coal is surrounded by 0.5 meters of solid coal on each side to form a 2m x 2m x 2m simulation domain. By combining both rubblized as well as solid pieces of coal in one simulation, we can directly compare the rates of heating which occur inside the simulation domain. For our current simulation, the bottom plane of the simulation is assumed to be a planar heating source with a constant temperature of 700 K.

During the previous quarter we encountered difficulties meshing the simulation domain. As mentioned, after removing and not accounting for the pipe heating element and replacing it with a planar heating element at the bottom of the simulation domain, we were able to successfully mesh the geometry. Figure 40 to Figure 43 show details of the mesh. As can be seen, the mesh is coarser in the solid piece of coal, with decreasing sizes to represent the rubblized coal pieces, and with the smallest cell sizes representing the fluid void between the pieces of coal. In total, the mesh has 110 million cells.
Figure 40. Mesh used to resolve individual pieces of coal.

Figure 41. Close-up of the mesh for one piece of coal.
Figure 42. Cross-sectional plane showing cell size distribution throughout the simulation domain. The outer, large cells are used to represent the solid block of coal, whereas finer mesh is used to resolve the individual pieces of coal and fluid occurring between the pieces of coal.

Figure 43. Close-up of the very fine mesh used to capture the fluid movement inside the convective channels which occur between the pieces of coal (which are colored in solid white color in this figure).
To capture, analyze, and compare the heat transfer rates for both solid and rubblized pieces of coal, we have created a plane with 100 by 100 points at which we capture temperature as a function of time. In effect, these points represent probes that are dispersed throughout the simulation domain and will allow us to compute the effective thermal conductivity as a function of void space for the simulation. These probes can be seen in Figure 44. This simulation is currently being run using our operator splitting algorithm. However, because of the large mesh needed to resolve the very fine geometric detail, this simulation is still in progress.

![Figure 44](image.png)

*Figure 44. Temperature probes inside the simulation domain.*

**CO₂ Adsorption**

*Completed Data on Raw Coals.* The data set for the raw coals has been completed. The raw coals included the Skyline (Utah), Carlinville (Illinois), and Powder River Basin (Wyoming). The experimental matrix for the raw coals involved two isotherm measurements at temperatures of either 50°C or 70°C using either CO₂ or methane as the adsorptive. The experimental matrix for the raw coal isotherms is displayed in Table 11.
Table 11: Experimental matrix showing parameters to the Langmuir adsorption equation for the untreated coals used in this study.

Table 11 also shows the fitting parameters for the measured data to the Langmuir adsorption isotherms equation:

$$V = V_\infty \frac{P \beta}{(1 + P \beta)}$$

In the Langmuir equation, $V$ is the volume of gas adsorbed in standard cubic feet (SCF) per ton, $V_\infty$ [SCF] is the theoretical maximum amount of gas that can be adsorbed, $P$ is the pressure in PSI, and $\beta$ [1/PSI] determines the shape of the isotherm. Isotherms for the untreated coals can be found in Figure 45.
Figure 45: CO₂ and methane isotherms for the untreated coals investigated in this study.

From the isotherm measurements on the raw coals, it can be seen that the PRB coal has the highest potential gas content in nearly every measurement, Illinois coal and Skyline coals have similar gas storage capacities which is to be expected as they are also similar in rank (bituminous and sub-bituminous, respectively). As expected, the gas content decreases with increases in temperature and storage capacity is higher with CO₂ than methane.

**Completed Data for Skyline coals treated at 0.1°C/min.** The data set for the Skyline coals treated with a heating rate of 0.1°C/min has been completed. The overall trend is consistent with previously reported data concerning the same coal being treated with a heating rate of 10°C/min. The trends are summarized as follows:

- Typically, gas content increases from coals treated to a higher final treatment temperatures: 325°C < untreated coals < 450°C < 600°C
- The decrease in gas content for coals treated to 325°C may be the result of fewer meso- and micropores as reported in the previous quarterly report.
- Gas adsorption decreases with increasing temperature
- CO₂ content is greater than methane

The Langmuir parameters for fitting the Skyline coals treated at 0.1°C/min can be found in Table 12. Plots of the measured data can be found in Figure 46.
Table 12: Langmuir parameters for the Skyline coals treated with a heating rate of 0.1°C/minute.

<table>
<thead>
<tr>
<th>Coal</th>
<th>$V_\infty$</th>
<th>$\beta$</th>
<th>$V_\infty$</th>
<th>$\beta$</th>
<th>$V_\infty$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>@ 50°C</td>
<td>@ 70°C</td>
<td>@ 50°C</td>
<td>@ 70°C</td>
<td>@ 50°C</td>
<td>@ 70°C</td>
</tr>
<tr>
<td>Skyline</td>
<td>842.7</td>
<td>634.9</td>
<td>1140.8</td>
<td>870.9</td>
<td>0.001359</td>
<td>0.001672</td>
</tr>
<tr>
<td></td>
<td>0.005929</td>
<td>0.004474</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>325@0.1</td>
<td>683.0</td>
<td>692.1</td>
<td>971.1</td>
<td>772.4</td>
<td>0.001393</td>
<td>0.001243</td>
</tr>
<tr>
<td></td>
<td>0.006026</td>
<td>0.006006</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>450@0.1</td>
<td>878.7</td>
<td>866.9</td>
<td>1136.5</td>
<td>913.4</td>
<td>0.002403</td>
<td>0.001846</td>
</tr>
<tr>
<td></td>
<td>0.01161</td>
<td>0.009927</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600@0.1</td>
<td>1234.6</td>
<td>1304.5</td>
<td>1493.9</td>
<td>1321.1</td>
<td>0.00451</td>
<td>0.003667</td>
</tr>
<tr>
<td></td>
<td>0.0203</td>
<td>0.013133</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Skyline Adsorption Isotherm 50°C w/ CH₄](image1)

![Skyline Adsorption Isotherm 70°C w/ CH₄](image2)
Figure 46: Adsorption isotherms for Skyline coal treated to various temperatures with a heating rate of 0.1°C/min.

The results of this study have implications for CO₂ injection post-treatment. It is obvious that for the sake of sequestering CO₂, higher treatment temperatures are preferable. Also, if the permeability in these coals are in any way related to the mesopores, there may be a region in the thermally treated coal that reached low treatment temperatures that may be resistive to CO₂ plume migration.

Completed Data for Illinois Coals Treated at 10°C/minute. The isotherm data set for the Illinois coals treated with a heating rate of 10°C/minute was also completed. Interestingly but not unexpectedly, the thermally treated Illinois isotherms show the same trends as the thermally treated Skyline coals. BET and Pore Size Distribution (PSD) data has yet to be completed on these coals to verify a correlation between meso- and microporous volume and gas storage capacity. The Langmuir fitting parameters for the Carlinville (Illinois) coals can be found in

Table 13. Plots of the gathered data can be found in Figure 47.
Table 13: Langmuir parameters for Carlinville (Illinois) coals treated with a heating rate of 10°C/min.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Fit</th>
<th>( V_\infty )</th>
<th>( \beta )</th>
<th>( V_\infty )</th>
<th>( \beta )</th>
<th>( V_\infty )</th>
<th>( \beta )</th>
<th>( V_\infty )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carlinville</td>
<td></td>
<td>760.3</td>
<td>0.001873</td>
<td>810.2</td>
<td>0.00147</td>
<td>1209.0</td>
<td>0.00567</td>
<td>1001.7</td>
<td>0.00441</td>
</tr>
<tr>
<td>325@0.1</td>
<td></td>
<td>846.8</td>
<td>0.001441</td>
<td>660.9</td>
<td>0.001451</td>
<td>1203.1</td>
<td>0.004547</td>
<td>899.8</td>
<td>0.004634</td>
</tr>
<tr>
<td>450@0.1</td>
<td></td>
<td>793.5</td>
<td>0.002139</td>
<td>847.2</td>
<td>0.001885</td>
<td>1017.0</td>
<td>0.009518</td>
<td>1022.2</td>
<td>0.008245</td>
</tr>
<tr>
<td>600@0.1</td>
<td></td>
<td>1034.5</td>
<td>0.005471</td>
<td>979.0</td>
<td>0.002856</td>
<td>1211.0</td>
<td>0.009124</td>
<td>1018.9</td>
<td>0.011249</td>
</tr>
</tbody>
</table>

![Illinois Adsorption Isotherm 50°C w/ CH₄](image1)

![Illinois Adsorption Isotherm 70°C w/ CH₄](image2)
Figure 47: Isotherm plots for the Illinois coals treated with a heating rate of 10°C/min. Trends in the adsorption isotherms mimic those seen with the Skyline coals.

It should be noted that some of the high-pressure data points were not included in the fitting of the data. These points were omitted because of leaking between the reference cell and the sample cell during the equilibration step of the isotherm measurement. These nuisance leaks, the result of a failing valve, do not seem to occur at lower pressures (<1200 PSI) and in most instances are not detected until pressures greater than 3000 PSI are applied.

Task 7.0 – Mercury Control

This task is complete.

Task 8.0 – Strategies for Coal Utilization in the National Energy Portfolio

8.1 Regulatory Promotion of Emergent CCS Technology

Work continued this quarter on drafting the topical report began this quarter.

8.2 Emerging Legal Issues for CCS Technology

This subtask is complete.
Task 9.0 – Validation/Uncertainty Quantification for Large Eddy Simulations of the heat flux in the Tangentially Fired Oxy-Coal Alstom Boiler Simulation Facility

Subtask 9.1 – LES simulation and V/UQ for heat flux in Alstom oxy-coal-fired BSF

Scaling test on Titan. In order to acquire the best computational performance and to optimize the number of processors for each case, scaling tests were conducted for two cases. The first case is a coal channel flow; the channel dimension is \(3m \times 3m \times 13m\) rectangular box, which is similar with the BSF simulation domain. The difference is that complex inside blocks were removed so that pure channel flow is formed. Coal and oxidizer were introduced from the bottom of the channel, no particle sources were considered for the gas phase so that the simulation was simplified. The second case is the real BSF simulation, all boundary conditions and inlet conditions were the same as the experimental conditions.

Both strong scaling an weak scaling analysis were evaluated for these two cases, and the results are shown in Figure 48 and Figure 49. In these two figures, each dashed line in horizontal represents a weak scaling test for a given processor load per processor. As processor numbers increase or as the case scales up, the wall CPU time per timestep for the simple channel flow remains the same. That means the case can be scaled up by using higher mesh resolution and more processors; as long as the mesh load per processor doesn’t change, the parallel computation efficiency doesn’t change. The strong scaling results are shown by solid lines. A solid line represents a given simulation case computed by different number of processors. The result for the channel flow also shows that a perfect strong scaling results were acquired.

![Figure 48. Scaling test for coal channel flow.](image)

For real BSF cases, however, both strong scaling and weak scaling results shows that computation efficiency will drop as the processor number increases. For example, the blue solid line represents the strong scaling performance for the 2cm resolution BSF case. As processor number increase from 620 to 3472, the wall CPU time per step only drops from 13s to 6s. This result shows that the parallel...
computation efficiency drops quickly as the simulation scale increases. The reason that scaling performance is not good for the BSF simulation is due to the complex flow field and the boundary conditions. Our CPU profiling results shows that PressureSolver will cost most of the CPU time in the BSF simulation. In Arches the pressure solver is solved by the parallel package Hypre, the performance of Hypre dominates such scaling performance. The best performance of Hypre can be acquired under a CPU load of $40^3$ cells/patch while in this test, the CPU load cannot be so high due to the limitation of the large CPU cost for each case. Based on the scaling test results provided by Figure 49 and the total CPU time that is needed for each case, the optimized simulation scale is identified as follows:

- 2cm resolution cases: 2008 processors for each case with a processor load of $20.4^3$/processor. The simulated total CPU time is 1.5M CPU hours on Titan.
- 1cm resolution cases: 9920 processors for one case with a processor load of $23.8^3$/processor. The simulated total CPU time is 14M CPU hours on Titan.

Figure 49. Scaling test for BSF cases.

**Effects of wall Boundary conditions.** Arches typically uses a combined MPM method to deal with wall boundary conditions. When we performed scaling tests for the BSF, we found that MPM components do not scale well for parallel simulation. For example, the MPM components only cost less than 0.5% of total CPU hours for 1-processor simulation. However, it will cost more than 10% of total CPU hours in a 1240 processors simulation both on local cluster Ember and on Titan. In order to improve the parallel efficiency and to save more CPU time, wall boundary conditions were developed in the Arches and are compared with the previous MPM models.

The wall stress can be calculated by
\[ \tau = (\mu + C_t \mu_t) \frac{\partial u_i}{\partial x_j} \]  

\text{Equation 9.1.1}

where \( \mu \) is the laminar viscosity, \( \mu_t \) is the turbulent viscosity and is calculated by Smagorinsky model. \( C_t \) is the coefficient of turbulent viscosity and needs to be verified. A channel flow BSF case was adopted to compare the effects of wall models. The simulations were conducted on local cluster Ember, and each case is calculated based on 12 processors. The vertical velocities under different wall models at 4s and 8s were shown in Figure 50 and Figure 51. Five simulation cases were simulated and shown as (a) to (e). And the description of wall model for these cases are listed as follows:

a) The previous MPM wall models, where wall stress is calculated in MPM model.
b) Assume that wall is non-viscous, so no wall stress is considered in Slip wall model.
c) Only consider the laminar viscous effect.
d) & e) to consider the turbulent viscosity in the wall model, with different weights.

As \( C_t \) increases, the effect of turbulent viscosity has a stronger effect on the wall model. The comparison in Figure 50 shows that a high \( C_t \) can lead to an unphysical vertical velocity, as high as 104m/s. However when \( C_t \) is less than 0.05, the results are reasonable and similar to the previous results acquired with the MPM wall model. Actually, the previous wall model didn’t consider the wall stress effect on the development of the flow field, which based on a no-viscous smooth wall assumption. As turbulent effects on wall stress were considered, as is shown in Figure 50 and Figure 51, the vertical velocity is similar to the previous model or slip wall model at first. However, as flow develops with time, the vertical velocity profile for case-E is different from slip wall models. The horizontal intersection velocity profile for case-E is smooth. The conclusion is that turbulent viscosity effects should be considered, and a coefficient \( C_t \) of 0.03–0.05 is recommended. In our BSF simulation on Titan, a \( C_t \) of 0.04 was adopted.
Figure 50. Contours vertical velocity at t=4s for different Wall BC models.

Figure 51. Contours of vertical velocity at t=8s for different Wall BC models.
**Code efficiency improvement.** In past three months, more effort focused on improving the LES calculation efficiency especially for large-scale parallel simulation cases. The code efficiency has been improved by at least 30% with the following conclusions:

- In pressure solver procedure, the matrix coefficient for the Hyper solver is only calculated in first time step and stored in following time step, rather calculating the coefficient every time step.
- Removing the MPM component and adding the wall model to Arches LES model is very important for heavy duty parallel simulations.
- Optimizing the iteration schemes for the coal oxidation model avoids the load imbalance in parallel computation and improves the efficiency. For example, Table 14 shows the computation tasks that cost the most CPU time for different processors for a 1240-processor parallel BSF simulation case on local cluster Ember and on Titan. On different processors, the char oxidation model will cost different times due to different iteration demands. In particular, this computation task will cost about 30% of total CPU time on some processors while only costing 5% of total CPU time on most other processors. This imbalance would cause all other processors wait for these few processors. An optimized iteration method guarantees that the coal oxidation model costs no more than 5% of total CPU time on any processor and thus saves a large amount of waiting time for parallel computations. As a result, this optimization saves 20% of total CPU time costs.
- Optimizing the simulation procedures in order to accelerate the total simulation process. For example, to use the small chemistry table and 4-flux radiation model at the beginning time step, to close the wall heat transfer model initially. As the LES simulation for the BSF evacuates all initial conditions and establishes the flow field, more accurate modes such as find-grid chemistry table and 8-flux radiation modes will be used to acquire more accurate results.

| Table 14. CPU profile for different processors on Ember and Titan for a 1240 processor BSF LES simulation |

<table>
<thead>
<tr>
<th>Processor</th>
<th>Task</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ember 0</td>
<td>Task Hyper Matrix solve (CC)</td>
<td>139.73126</td>
</tr>
<tr>
<td>Ember 100</td>
<td>Task Hyper Matrix solve (CC)</td>
<td>139.73126</td>
</tr>
<tr>
<td>Titan</td>
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LES tests on Titan. After the strong scaling and weak scaling tests on Titan, as described in the first subsection, the optimized processor numbers for 2cm and 1cm cases have been identified. These two cases are running on Titan now. We do not have any new results, but expect additional results in next quarterly report.

Subtask 9.2 – LES simulation and V/UQ for heat flux in subscale UofU oxy-coal-fired OFC

The radiation model is important for heat flux simulation. In order to use GPU in parallel simulations and to test newly developed RMCRT radiation model and radiation property model. LES simulation for the oxy-coal-fired OFC was conducted with three different radiation methods as follows:

- DO radiation model with old radiation property calculation method which interpolate the Hottel chart curve fit, which is symbolized as “DO_1”
- DO radiation model with newly developed radiation property calculation method with Planck Mean Absorption Coefficients, which is symbolized as “DO_new”
- RMCRT radiation model with new radiation property calculation method, which is symbolize as “RMCRT”.

Since this study is used to test radiation results, the dimension of the simulation domain is a cylinder with a 1m height and a 0.2m diameter, which is smaller than the OFC experimental test rig, and is shown in Figure 52. The primary flow is composed by 36.6% of O₂ and 63.4% of CO₂ and the temperature is 424K. The secondary flow represents the mixture of O₂ and the hot recycled flue gas, and the composition is 15.8% of O₂, 81.9% of CO₂ and 2.3% of H₂O with a temperature of 1000K. Coal particles were entrained into the furnace by the primary flow. The surrounding hot flue gas will heat up the coal particles quickly, so that flames are formed in the furnace.

The instantaneous simulation results of temperature and absorption coefficient under different radiation models are shown in Figure 53 and Figure 54. The temperature profile predicted by RMCRT is higher than the results with DO radiation model. The new predicted gas absorption coefficient is smaller than “Hottel’s chart curve fit” method. While the new predicted particle absorption coefficient is larger than the old model. The DO radiation model has been verified, and the RMCRT radiation model needs further study.
Figure 52. Simulation domain of OFC for radiation model evaluation.

Figure 53. Predicted temperature under different radiation models.

(a) $t=0.12s$  
(b) $t=0.02s$
The investigators are also organizing a summary of experimental OFC data for the V/UQ efforts.

**Subtask 9.3 – IR camera diagnostics & V/UQ for Temperature measurements in UofU OFC**

We used three different cameras to obtain the multi-channel data: a mid-wave infrared (MWIR), a high-speed visible (VIS) and a color CMOS camera. The properties and setup parameters of the cameras were the following:

- **MWIR**
  - Camera type: FLIR SC6703
  - Frame rate: 10
  - Integration time: 0.2 ms or 5 ms
  - Filters used: MWIR neutral density, divide by 1000, 3-5 m wavelength
  - Single frame mode, noise suppressed readout
  - Lens: narrow-angle MWIR lens to reduce glare and reflections (F# 2.4)
  - Bit depth: 14 bit, grayscale

- **VIS**
  - Camera type: Photron APX-RS
  - Frame rate: 2000 or 10
  - Integration time: 0.2 ms or 5 ms
  - Filters used: visible neutral density, divide by 2, 4 and 8, 0.3-0.7 m wavelength
  - Dual frame mode, the frame rate was 10/2000 (single frame/dual frame)
  - Lens: Tamron telephoto lens (F# 11 and 5.6)
  - Bit depth: 10 bit, grayscale

- **Color camera**
  - Camera type: EPIX CMOS SV5C10
  - Frame rate: 10
The cameras were aligned so that they saw approximately the same area of the inspection window on the furnace. The distances of the cameras from the central axis of the flame were between 2 m and 3 m.

The image processing, image registration and camera calibration steps were described in previous reports. The information in the color images were used to extract temperature and soot concentration profiles. This was done based on the thesis work of Teri Draper (2012).

The flames were all produced by a co-axial burner. The overall fuel-air equivalence ratio of the flames was kept constant, but oxygen was introduced differently in the different cases. The oxygen concentration in the primary oxidant stream varied between 0-20%. For details, see the quarterly reports for Task 3.2. This approach allowed us to study the effect of varying local equivalence ratios. Three different coals were tested: Utah Skyline bituminous, Illinois #6 and Powder River Basin (Black Thunder).

The two-color method combined with infrared-visible temperature measurement described in the previous quarterly report was tested, and it was found that the separation of soot radiation to a visible and mid-wave infrared channel is not possible in the case of the studied flames, due to the interference caused by hydrocarbon radiation. Thus, the infrared and high-speed video data were only used to calculate heat flux within narrow and wide visible and mid-wave infrared bands. Temperature and soot concentration information were obtained by the color imaging method.

Figure 55 presents an example of results. This subset of results is for the 20% oxygen concentration case, for all three studied coals.

Since the initial chemistry of the flame was constant during these experiments, the differences in radiation profiles are caused by the differences between coal types. Flame radiation may be indicative of reaction kinetics in the flame, if the de-coupling of flow and chemistry effects can be done to some extent. For this purpose the high-speed camera was used to extract flame velocities. The technique applied for this task was described in previous reports. A paper describing this methodology has also been submitted to the journal Experiments in Fluids. Flame velocities are shown in Figure 56.
Figure 55: Extracted axial profiles of visible (first column), infrared (second column) heat flux, temperature (third column) and path-integrated soot concentration (fourth column). The rows show results for flames of Utah bituminous coal (top row), Illinois #6 coal (middle row) and Powder River Basin coal (bottom row). The axial coordinates are in meters.

Figure 56: Obtained two-dimensional flame velocity magnitude maps. Spatial coordinates are in millimeters, and the color scales have units of m/s.
The de-coupling of flow and reaction phenomena has not been completed. It was found that the obtained velocity maps are inadequate for this purpose, due to missing data in locations where the flame had little visible intensity.

When analyzing the color images, it was also found that the color camera method of Teri Draper (2012) produced unstable numerical solutions of the emission equation, leading to highly uncertain measurements. The reason was identified as the highly overlapping spectral response curves of the used CMOS sensor.

To address these issues, another set of tests has been planned, in which both the high-speed visible and MWIR camera will be used to extract velocity information. The MWIR camera can detect moving flame features in areas, which are too dim for the visible camera, thus it allows for the extraction of apparent velocity in the problematic areas as well. To address the problem of overlapping spectral response curves, a beam splitter is being built, with which truly narrow band two-color measurements can be made. This new set of tests is scheduled in early August.

Subtask 9.4 – Heat flux profiles of UofU OFC using advanced strategies for O$_2$ injection

The student working on this subtask focused on completing subtask 3.6 this quarter.

CONCLUSIONS

**Oxy-coal combustion.** During this quarter, the Oxycoal Team studied the effect of recycle cleanup options on PSDs and found that it did not affect PSDs significantly.

**Gasification.** Entrained particles can now be represented in the discrete ordinates radiation model. Verification testing of the calculation and handoff of radiation properties was performed, and favorable results were obtained. In addition, characterization of sprays with a variety of particle size loadings and fuels indicates that the spray dynamics are complex functions of both the atomizer design and the slurry properties. Some trends in drop size and spray direction have been identified with this particular atomizer design along the center axis of the spray, but extending them to the edge of the spray is not as straightforward. The geometry of the atomizer is suspected to play a part in the dynamics at the edge of the spray, as some liquids are prone to forming drops along the atomizer’s bottom face.

**CLC.** The investigators presented a framework for sensitivity analysis in modeling of polydispersity in a fluidized bed. They evaluated the effects of polydispersity in fluidized beds for three different techniques: monodispersion, finite-dispersion, (polydispersity), and DQMOM. Preliminary results showed that a slight improvement was obtained by including polydispersity in the fluidized bed modeling. In addition, the oxidation kinetics for Cu$_2$O on two different oxygen carriers were determined. At high temperatures comparable to those expected in industrial chemical looping systems, modeling pore blocking during oxidation was found to improve the fit to experimental data. Because of the differences seen between the predictive model and the observed kinetics it is possible that there is not a universal rate law to describe all copper-oxide based oxygen carriers and that the true kinetics might need to be determined on an individual basis. The models used, however, do adequately describe the observed characteristics of the materials tested. Small-scale testing of solid fuel conversion demonstrated that it is possible to fully combust solid fuels without the need for a slow gasification step. The final design of chemical looping...
systems will have to balance the oxygen release rate with the fuel conversion rate so that the effluent from
the fuel reactor does not contain unreacted volatile material or unreacted oxygen.

**UCTT.** Duplicate coal pyrolysis experiments revealed similar gas yields but distinct differences in the
liquid to gas ratios compared to previous studies. The reason for these differences is still unclear, and
more tests need to be performed to provide explanation. In addition, data sets were completed for the
untreated Skyline, Carlinville, and Powder River Basin coals. Furthermore, data sets for the Skyline coals
being treated with a heating rate of 0.1 °C/min and Carlinville coals being treated at 10 °C/min have also
been completed. The trends in both of these data sets are consistent. Gas capacity decreases for samples
treated to 325 °C relative to the untreated coals and increases for coals treated to temperatures exceeding
450 °C. The injection implications of this decrease may be a zone in reduced adsorptive capacity and
possible reduced permeability at some distance from the heater.

**V/UQ for LES of the heat flux in the tangentially fired oxy-coal Alstom boiler simulation facility.** The
strong and weak scaling studies of the BSF simulations revealed that computation efficiency drops as the
processor number increases. The reason that scaling performance is not good for the BSF simulation is
due to the complex flow field and the boundary conditions. Our CPU profiling results shows that
PressureSolver is responsible for must of the CPU cost time. The investigators also focused effort on
improving the LES calculation efficiency especially for large-scale parallel simulation cases, and
improved it by approximately 30%.

**MILESTONE STATUS**

Table 15 summarizes the key milestones.

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<th>Actual Completion Date</th>
<th>Notes</th>
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<td>June 2011</td>
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<tr>
<td>Proof of concept OFC demonstration of coaxial segregated/directed O₂ injection</td>
<td>August 2011</td>
<td>August 2011</td>
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<tr>
<td>Characterization of gasifier at 15 atm</td>
<td>December 2011</td>
<td>June 2012</td>
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<td>Preliminary dataset including thermo-chemical parameters from the lab-scale test facility</td>
<td>June 2012</td>
<td>June 2012</td>
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<tr>
<td>Summarize lessons learned from BSF simulations</td>
<td>July 2013</td>
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**Completed milestones**

Subtask 4.3. Optimization of code and implementation of entrained coal particles.

**Delays/Problems with upcoming milestones and deliverables**

Subtask 5.2. Sensitivity analysis of HPC simulations for an experimental CLC bed with no reactions
using literature data. Completion of this milestone has been delayed because the clusters, which are used
to perform the simulation studies, along with the facilities that house these clusters, were serviced and therefore unavailable for longer than expected timeframe during the last quarter. The investigators have completed a preliminary sensitivity analysis and expect to complete this milestone in August 2013.

Task 6. Demonstrate simulation tools & preliminary V/UQ. This milestone is delayed while the investigators wait for experimental data from the rubbliezed-bed reactor. These experiments have not begun, and we anticipate completing these by December 2013.

Subtask 9.1. Summarize the lessons learned from the BSF simulations that would apply to Alstom's design of a 350 MWe oxy-coal demonstration, originally due June 2013. This milestone will be delayed due to delays in obtaining experimental data for the V/UQ studies and Titan’s unanticipated downtimes. We anticipate completing this milestone by July 2014.

Subtask 9.2. The upcoming milestone, complete V/UQ simulations and analysis for temperature and heat flux in the OFC, due June 2013, will be delayed while we wait for experimental results. We anticipate completing this milestone by October 2013.

Subtask 9.3 IR camera diagnostics & V/UQ for temperature measurements in OFC will be delayed. The investigators obtained an extensive dataset on the OFC for the parameters of relevance to Task 9 and the completed an analysis of that data in June. They now have spatial heat flux and temperature information for 3 coals, each under several different conditions. The investigators feel that additional modifications to our procedure could provide greater accuracy for temperature measurements. Additional equipment needed for these improvements should arrive in early August, and another test campaign is schedule in August to try the modified approach. We should have this effort completed by the end of September, 2013.

ACCOMPLISHMENTS
The CLC team developed and verified models for the oxidation of Cu₂O in two different oxygen carriers.

COST PLAN
The cost plan can be found in the attached appendix.

REFERENCES


RECENT AND UPCOMING PRESENTATIONS/PUBLICATIONS


Sahir, A.H.; Sohn, H.Y.; Lighty, J.S., A fluidized bed model of the fuel reactor for a Chemical Looping with Oxygen Uncoupling process, Abstract communicated for presentation at the 8th US National Meeting of the Combustion Institute, Salt Lake City, UT.


