(19) The Use of Real Time Measurement and Artificial Intelligence to Improve Efficiency and Reduce Emissions at Coal-Fired Power Plants

This two-year effort will seek to develop a technique to measure coal properties in real time, and to process the data such that coal-fired electric utility operators can adjust their operation to avoid slagging and fouling.

Total project cost: $750,000
Funding request: $600,000
Project Lead: NYSERDA
Project Participants: Brayton Point Generating State; Energy Research Company; Lehigh University

Start Date: August 1, 2005
End Date: August 1, 2007

Patents

None.

Progress in Past Quarter and Current Status

Instrument Modification

The primary modification to the coal analysis equipment consisted of improving the control of the purge gas to the measurement chamber. During the analysis of materials, argon or helium is used as a purge gas. The LIBS spectra collected from materials in the chamber show strong spectral lines from these gases and the tails of these lines overlapping the spectral lines of the elements of interest, specifically oxygen and potassium. Variations in the purge gas pressure can lead to fluctuations in the intensity of the tails from purge gas spectral lines and thus the background of the spectral lines from the elements of interest. Therefore, greater control of the purge gas pressure should increase the consistency of the analysis from the spectral lines.

In the past, the purge gas flow to the chamber was controlled by needle valve and the pressure determined with a gauge with a resolution of 1” of Hg. Further, the flow rate of the purge gas was not monitored. To improve the purge gas control, a pressure gauge with a 0.01” of Hg resolution and a rotameter with a range of 4 to 40 SCFH were installed. Further, the rotameter is equipped with a 10 turn needle valve for flow control.

The current valve was left in the system as a purge gas on/off valve. During measurements, this purge gas system allows for the gas pressure to be controlled to +/- 0.05” of Hg and the flow setting to remain unchanged between samples. Further the flow to obtain a given pressure can be accurately monitored.

LIBS Analysis

Chemical analyses of materials for the C, O, H, S, K, and N using the photodiodes and the chamber have been initiated. This work included establishing the sample preparation requirements, measurement on coal surrogate materials and initial analyses on coal samples.

Sample Preparation Methods

Coal samples are potentially difficult to analyze with LIBS due to their inhomogeneous nature. Grinding the samples to a fine powder improves the homogeneity but leads to further difficulties due to the scattering of powder (dusting) during the LIBS measurement. To address these problems, sample preparation methods were investigate during this quarter.

To address problems with homogeneity, the procedure for grinding the coal samples to a fine powder was developed. Initially, the coal samples were ground with a mortar and pestle and the resulting powder was then past through a 100 mesh sieve. Material remaining on the screen was reground and sieved. This procedure was repeated to until the whole sample past through the sieve. This insured that the complete sample was a fine powder with a particle size less than 100 mesh and the element composition of the original sample preserved.

To address the dusting problems from powder samples during the LIBS measurements, pressing the powders into disks and the use of double sided sticky tape were investigated.

These potential sample preparation methods were selected based on experience and a review of the LIBS literature relating to the analysis of powder samples.

Pressed disks were prepared by mixing the ground coal samples with 10-20 wt% KBr and then pressing the powder in a die with a pressure of ~1000 psi. The KBr was added as a binder to increase the strength of the bonds between the particles. The resulting pressed disks were ~3" in diameter with a thickness of 1/8". The die was designed such that the die and disk could be placed into the measurement chamber without the removal of the disk from the die. This prevented the breaking of the disk in the removal process. The suitability of the pressed samples was assessed by colleting LIBS spectra from the sample and assessing the amount of dusting and damage to the disk. During these tests, it was observed that a significant amount of dust was generated and several of the disks cracked into smaller pieces.

Double sided sticky tape samples were prepared by first mounting the double sided sticky tape on an aluminum piece. The protective sheet was then removed from the tape and the ground powder placed on the tape. The powder was spread over the tape with a plastic spatula and the excess material removed through lightly scraping the surface and tapping the aluminum piece on a hard surface. Again the initial suitability of the sample preparation method was determined by collecting LIBS spectra from the prepared samples. These test showed a significant decrease in the dusting during the laser shots.

Further C,O, and H LIBS analysis on powder organic compounds with known compositions showed a good correlation between the reported and measured compositions.

Based on the dusting and fracturing problems with the disk samples and the decreased dusting and the LIBS analysis results on organic compounds, the use of double sided sticky tape was selected for mounting samples.

Analysis of Surrogate Materials

Experiments were performed to determine the effectiveness of the photodiodes for determining the C, H, O, and N compositions. These experiments were performed on coal surrogate samples prepared from purchased chemicals. The preparation of coal surrogate samples allows for tight control over the sample compositions and eliminates the reliance on potentially poor or questionable compositions provided with coal samples.

In the first set of experiments, photodiode signals collected after a laser spark generated on an organic compound sample were compared to the compositions of organic compounds. The compounds were selected to have wide C, H, O and N composition anges. The compounds and mixtures used are listed in Table 1 while the resulting molar compositions are listed in Table 2.

The spectra analysis of these materials was performed by collecting photodiode traces under a -20” of Hg argon atmosphere. 20 traces were obtained from each sample while moving the sample between laser sparks to allow a fresh portion of the sample to test with each laser spark. The photodiode signals were determine by subtracting an exponential background signal from the element traces and then integrating over the time range of 1 to 4 µs. The exponential background signal was derived from a photodiode trace collected at 600nm.

To compare the photodiode signals to the sample compositions, the ratio of the photodiode signals to the C photodiode signal were plotted versus the molar ratio of the elements to carbon in the samples. The resulting correlations for potassium and oxygen are shown in Figure 1. The correlation between the C, K, O and H signals appears to be strong, while the correlation with the N 868 signal was much weaker. The poor correlation for the N signal was potentially due to the N 868 line being too weak to be observed or the N combining with C to form a CN.

Due to the position of the K 769 lines with respect to two strong argon lines, the impact of the purge gas atmosphere on the potassium photodiode signal was further investigated through measurements performed on KBr spiked antharacene samples. The samples were prepared by first grinding KBr to a fine powder and then mixing the KBr with the anthracene through additional grinding. The samples were then mounted on double sided sticky tape for analysis in the coal chamber with the photodiodes. 20 traces were collected from each sample. For select mixtures, duplicated samples were prepared to test the repeatability of the measurements. Traces were collected under argon and helium atmospheres with a pressure of -15 and -20” of Hg.

The traces were analyzed as previously described and the resulting correlation is shown in Figure 2. From this plot, it appears that the argon spectral lines near the K 769 lines have little impact on the correlation between the K/H photodiode signal and the molar K/H ratio. Therefore, the argon spectral lines and the tail wings from these lines are not expected to interfere with the analyses of other elements. Further, at these low concentrations with an atmosphere of -20” Hg, the K/H photodiode signals show a strong linear correlation with the molar K/H ratio.

Initial Coal Analyses

Initial analyses of coal samples spiked with sodium sulfate were performed to assess the ability of the S-921 filtered photodiode to detect sulfur. Samples were prepared by grinding sodium sulfate to a fine powder and then mixing with a coal sample previously reduced to minus 100 mesh by additionally grinding. The maximum sulfur concentration in these samples was on the order of 6 weight percent. The powder samples were then mounted on double sided sticky tape and photodiode traces collected from the samples.

The photodiode traces were collected under an atmosphere of -20” Hg.

The collected data was then analyzed as previously described to determine the S/C photodiode signal ratio. This ratio did not show a correlation with the molar S/C ratio determined from the coal composition and the amount of sodium sulfate added to the coal. Further analysis of the collected traces revealed that the O/C photodiode signal ratio did not correlate to the molar O/C ratio in the samples. The molar O/C ratio increase with the addition of sodium sulfate to the coal due to the oxygen in the sulfate ion. This discrepancy was investigated further by collecting emission spectra from the samples to observe the relative intensities of the H-656 and O-777 spectral lines. In the spectra collected, the intensity ratios of these lines did not change with sodium sulfate content in the sample.

Based on these results, it is hypothesized that insufficient coupling of the laser to the coal sample is resulting in decreased plasma temperatures. These lower plasma temperatures allow for the formation of molecular species that decrease the population of the monatomic species that lead to the expected spectral lines. This leads the poor correlation between the photodiode signals and the sample compositions.

Planned Work

During the next reporting period, the work will target extending the current analysis of materials from the surrogate materials to the actual coals and validating the measurements performed on coals. Specific planned activities include:

-validate photodiode system for determining sulfur content in materials through analysis of spiked surrogate materials.

-test poor laser sample coupling hypothesis for coal through comparison of surrogate and coal analyses of spiked samples.

-improve coupling of between laser and coal sample through changes in the laser/laser focusing component of the experimental setup.

-with improved experimental setup, develop calibration curves for coal samples using spiked samples.

-determine C, O, H, S, K, and N compositions for coal samples using photodiode system.

Evaluation of the experimental setup will continue to identify opportunities to improve the hardware and software to improve the raw LIBS data. Further, the development of the analysis method for the photodiode signal will continue.