ABSTRACT

Organic sulfur determination, as defined by ASTM, fails to provide a direct method of determination of organic sulfur in coal. The total sulfur is determined by the Eschka method (D3177-75), and the sulfate and sulfide by selective leaches (D2492-68). The organic sulfur is then calculated from the difference between the total and the two inorganic sulfur forms. The errors associated with existing indirect organic sulfur analysis derive from the summation of all the errors obtained from the total, pyritic and sulfatic sulfur data. The ISGS has developed and tested an approach to determine organic sulfur in coal and coal derived products. The approach was tested in the laboratory and found to produce results comparable to the ASTM method. Tests with Illinois Basin Coal samples showed that the ISGS method produced a good analysis precision compared with the ASTM method. The average difference between the results by the two methods is 5.16%, ranging from 2.12 to 7.25%. The direct method provides a possible alternative to the existing ASTM method and commercialization of this method could benefit the development of organic sulfur removal processes.

The objective of this project was to build and test an instrument for determination of organic sulfur based on the previous ISGS approach - selective oxidation of the organic fraction of a coal and quantitative analysis of the gases produced. The complete system consisted of an oxidation furnace unit and a gas analysis unit. The furnace was designed and built in collaboration with the electronic shop in the University of Illinois at Urbana-Champaign Department of Chemical Sciences. Tests showed that a selective oxidation was successfully carried out in the new furnace built in the ISGS. However, the existing ISGS Perkin Elmer (PE) elemental analyzer which was originally proposed to be tested for quantifying the gases produced, was not sensitive enough for SO₂ analysis. Also, an existing ISGS gas chromatograph (GC) equipped with both a flame photometric detector (FPD) and a thermal conductivity detector (TCD) was inadequate to quantify that the organic matrix of the coal was oxidized. Further testing using the GC with a reconditioned or a new FPD detector is recommended.
The ASTM methods can directly determine the total sulfur and the major forms of inorganic sulfur, pyritic and sulfatic. The ASTM organic sulfur is then obtained by difference between the amount of inorganic sulfur and the amount of total sulfur. At least two problems are associated with such organic sulfur determination with the ASTM method. First, there are forms of inorganic sulfur, such as monosulfidic sulfides, marcasite and elemental sulfur, that are not determined but are consequently included in the organic sulfur by calculation. Second, errors and uncertainty of analysis accumulate and cause the organic sulfur analysis to be the most uncertain. Uncertainty in organic sulfur analysis by the ASTM methods can be a particular problem when evaluating processes to remove organic sulfur from coal. It is important to provide an accurate analytical tool to evaluate the efficiency of a process for organic sulfur removal from high-sulfur Illinois coal.

The ISGS has developed and tested an approach to directly determine organic sulfur in coal and coal derived products based on the selective oxidation of organic sulfur in the coal. The approach was tested using a large ISGS existing device that could selectively oxidize the organic matrix in coal. This device was coupled with an ISGS existing quadrupole gas analyzer that could quantitatively determine the composition of the (sulfur) gases produced from the device. The tests with Illinois Basin Coal samples showed a good analysis precision compared with the ASTM method. The average difference between the results by the two methods is 5.16%, ranging from 2.12 to 7.25%. The direct method provides a possible alternative to the existing ASTM method and commercialization of this method could benefit the development of organic sulfur removal processes.

This study focused on the previous ISGS approach in developing an instrumental analytical technique for direct determination of organic sulfur in coal or coal products. The purpose of this study was first to build a small furnace. This specific furnace was much easier to handle during testing compared with the previous device. Also, other existing ISGS instrument were tested for quantitative analysis of the gases produced from the specific furnace. Successful results of this study depend on the constructed furnace to preferentially oxidize organic fraction of coal and also depend on the existing instrument to quantitatively analyze the gases produced under preferential oxidation.

The specific objectives of this study were to:

1. Conduct a literature search to reveal the method, if any, on direct determination of organic sulfur in coal and coal products, the technique to preferentially oxidize the organic fraction of coal and coal products, and the gas analysis technique for quantifying the gases produced.

2. Build a furnace and test the furnace for preferential oxidization of organic fraction of coal for organic sulfur in the coal determination through on-line gas analysis.

3. Modify and test an ISGS existing instrument for on-line quantitative analysis of gases
including sulfur-containing gases produced from preferential oxidization of the organic fraction of coal or coal products.

A literature search was conducted (Task 1) to reveal the method, if any, on direct determination of organic sulfur in coal and coal products, the technique for preferentially oxidize organic fraction of coal and coal products, and the gas analysis technique for quantifying the gases produced. The literature search confirms the feasibility of gasifying only the organic matrix of the coal while leaving the inorganic portion essentially unchanged. Upon complete removal of the organic material, oxidation of the mineral matter can occur, but that is not a problem. The instrument designed does not require complete removal of the organic matrix. One particularly interesting paper indicated that dilution of oxygen with helium in the furnace produced more controlled oxidation. This information leads to tests on ashing at atmospheric pressure in the specific furnace (built in Task 2).

Construction of a specific furnace (Task 2) was accomplished through a collaboration with the electronic shop in the University of Illinois at Urbana-Champaign School of Chemical Sciences. For organic sulfur in coal analysis, the furnace was attached to the existing gas analysis instrument and tested for its capability to selectively oxidize the organic fraction of coal by on-line quantitative gas analysis.

An ISGS existing instrument, Perkin Elmer elemental analyzer (PE240C) for CHN analysis, was first modified for CHS analysis (Task 3). On-line quantitative analysis of gases including sulfur-containing gases produced from preferential oxidization was conducted on the test samples. The PE240C was equipped with thermal conductivity detector (TCD) for gas analysis. The test results indicated that the TCD detector was not sensitive enough for sulfur-containing gases (SO\textsubscript{2}) detection. Also, it was not capable of detecting CO and SO\textsubscript{3} gases if they were produced. Therefore, a different ISGS existing instrument, Tracor 540 gas chromatograph (GC) was assembled. The Tracor GC equipped with both a flame photometric detector (FPD) and a thermal conductivity detector (TCD) was tested, instead of PE240C, for gases (CO, CO\textsubscript{2}, SO\textsubscript{2} and SO\textsubscript{3}) determination. The FPD was much more sensitive compared with the TCD detection, and it was specific for selective sulfur gases detection.

Overall, the results indicated that the oxidation conditions in the specific furnace was achieved but the GC was found to be inadequate to quantify the gases produced from organic matrix of the coal. Further investigation using GC with a reconditioned or a new FPD detector for gas analysis is recommended.

The remainder of this report contains proprietary information and is not available for distribution except to the sponsor(s) of this project.