Characterization of Coal by Thermal Analysis Methods

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Thermogravimetric analysis (TGA) is an instrument with immense utility for analyzing numerous coal systems. Although TGA instrumentation technology limits the heating rate, TGA is very useful in making valid predictions of the chemical and physical properties of coal. TGA's foremost advantages are the precision, speed, and ease that samples can be analyzed. One person can analyze small samples on the order of grams that would demand a larger staff and much more money to analyze in a large-scale combustion system.

Coal is a very heterogeneous material composed of both organic and inorganic substances. The organic contents called coal macerals are the desired portion of the coal. The inorganic contents called mineral matters are unwanted components that dilute the coal and provide a means for pollution that are undesirable. Coals can be classified by rank of the calorific value. Once the coals are ranked by the calorific value in BTU/lb., other qualities such as the volatiles content can be used to further divide the ranks into sub-categories. With increasing rank many important properties of the coal change. Specific qualities include increased size of hydrocarbon molecule, increased carbon content, increased calorific values, decreased water content, and decreased volatile content. Overall as the rank of coal increases, the quality and value of the coal also increases.

The combustion of coal is generally the combination of the two processes. One is the pyrolysis or devolatilization of the coal due to an applied thermal stress. The second is the heterogeneous combustion of the remaining char according to carbon-oxygen reactions. The ignition rate is very important when discussing the combustion of coal. High heating rates will cause simultaneous evolution and ignition of volatiles, whereas with low heating rates devolatilization will occur prior to ignition and combustion. The burning profile of coal can be an instrumental analysis in distinguishing between different coals. Four key characteristics of the DTG curve should be used when analyzing a burning profile. The initial temperature (IT) is the temperature at which pyrolysis is initiated. The fixed carbon initiation temperature (IT_{FC}) is the temperature in which combustion of the coal begins. The IT region and the IT_{FC} region overlap because releasing volatiles from the coal sample creates conditions encouraging combustion. The peak maximum temperature (PT) is simply the temperature at the peak of the DTG curve noting the temperature at which maximum weight loss occurs. The burnout temperature (BT) is the temperature at which the weight loss has ended and a baseline weight has once again been reached. Figure 1 shows each of the four previous discussed characteristics for a coal sample.

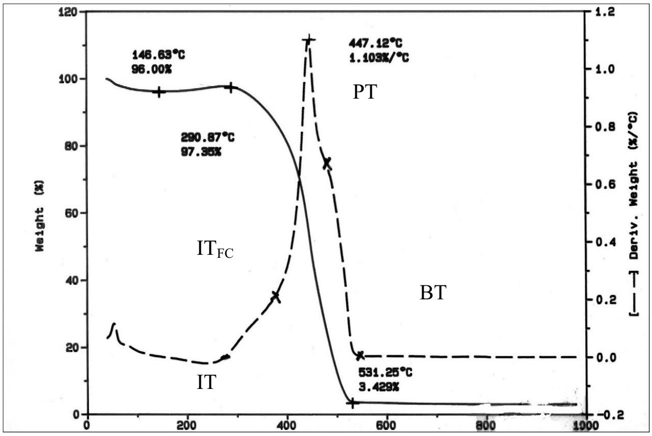

Figure 1. Characteristic Points on DTG Curve of Coal Sample

Coals of higher rank generally have a higher peak maximum temperature as shown by Figure 2.

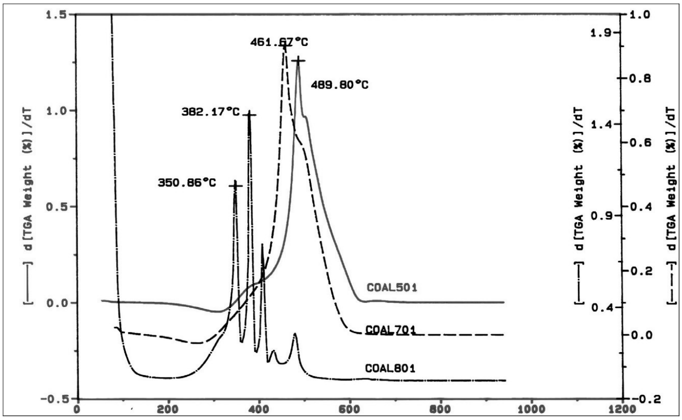

Figure 2. DTG Curves of Coal Samples of Various Ranks

This trend occurs because coals of higher rank contain less mineral matter effectively raising the calorific values. Figure 3 shows that the peak temperature follows a pattern as a function of carbon content.

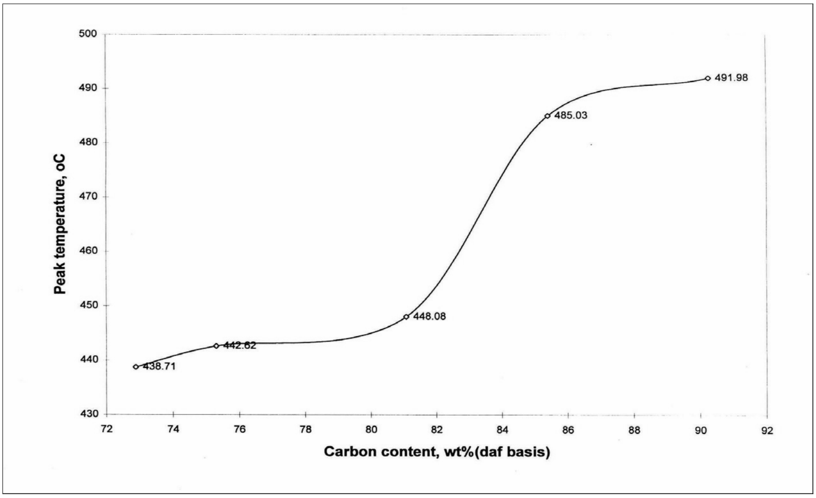

Figure 3. Peak Temperature as a Function of Carbon Content

For carbon contents in the range of 82-84%, the peak temperature would differ by a large amount. However, in the regions of 76-78% and 88-90% the peak temperature would vary by only a slight amount. The rate at peak temperature also follows a trend. Coals with 84-85% carbon content experience the highest rate at peak temperature; thus, burning more efficiently.

Proximate analysis is the determination of the moisture, ash, and volatile matter. ASTM standard methods have been written for proximate analysis. Figure 4 shows how TGA can be used to perform the proximate analysis of a coal sample.

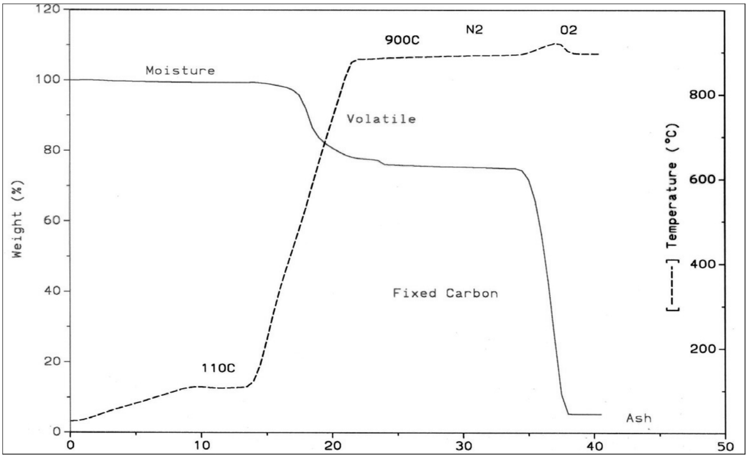

Figure 4. Proximate Analysis Using TGA

The furnace temperature is ramped to 110ºC and held isothermally. This ensures that any weight loss experienced is a direct effect of the moisture of the coal. The temperature is then ramped to 900ºC and held isothermally. Any weight loss occurring in this isotherm region is a direct result of the loss of volatiles. The previous two steps are performed in a nitrogen atmosphere. For the third part, the atmosphere is changed to oxygen. This creates an environment suitable for combustion. Once the coal is completely combusted, the residue is taken as the ash.

Coal blends are used to make coal burning more environmentally considerate. Coals having high sulfur contents can be blended with low sulfur coal to decrease SO_2 emissions, while retaining the efficiency. TGA is a very versatile instrument in assessing the feasibility of using coal blends. The linear additive rule can be used to estimate the theoretical composite value of a blend, but TGA must be used to estimate whether or not the properties of the blend are additive or not. A property is additive when the blend's physical property can be predicted by the relative amounts of the component coals and their physical properties. The linear additive rule is a relationship defined by the properties of a coal in a blend and the amount of that coal in the blend. A series of coal blends were studied under isothermal and non-isothermal conditions in order to determine what physical properties of specific coal blends are additive or non-additive [1]. Collectively the TG curves show that some TG parameters under non-isothermal combustion conditions are additive such as residue and weight loss while others such as peak temperature and maximum rate are not. For isothermal combustion the peak temperature and maximum rate are additive, while the residue and combustion end point temperature is not. TGA is utilized to such a great extent because TGA analysis of coal blends is fast, simple, and yields precise and accurate results.

Chlorine in the form of HCl in coal has the potential to generate chlorinated hydrocarbons that can be released into the atmosphere that may be capable of causing corrosion [2]. TG-FTIR and TG-MS show good correlation to the temperatures where HCl is evolved. Figures 5 and 6 are the TG-FTIR and TG-MS plots, respectively.

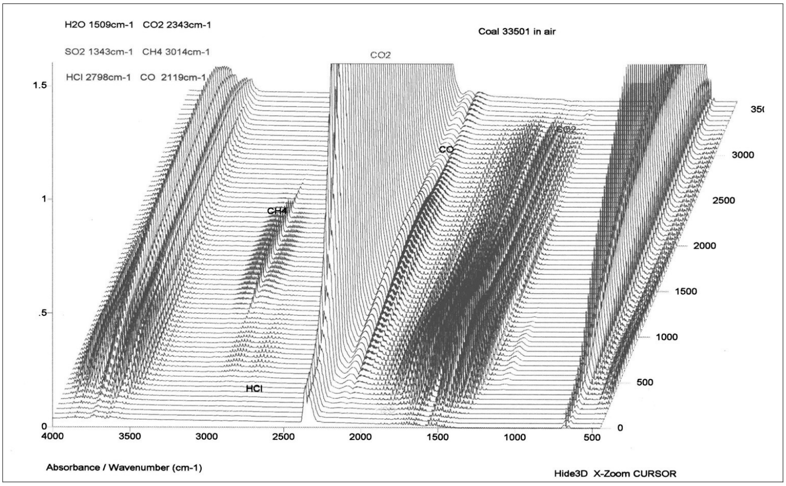

Figure 5. TG-FTIR of Coal Blend

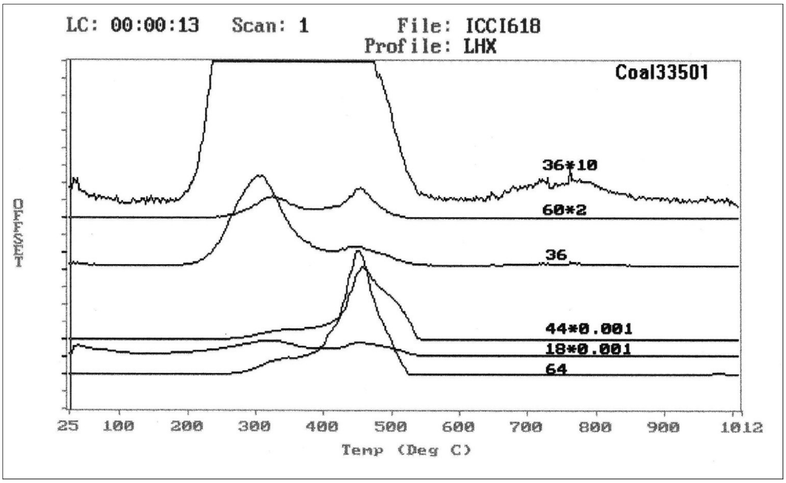

Figure 6. TG-MS of Coal Blend

However, the TG-MS plot shows that the HCl evolution appears to occur in three regions. Figure 7 shows that the amount of HCl and SO_2 released as determined by the integration of the FTIR curves correlate very well with the actual percentage of HCl and SO_2 of the coal.

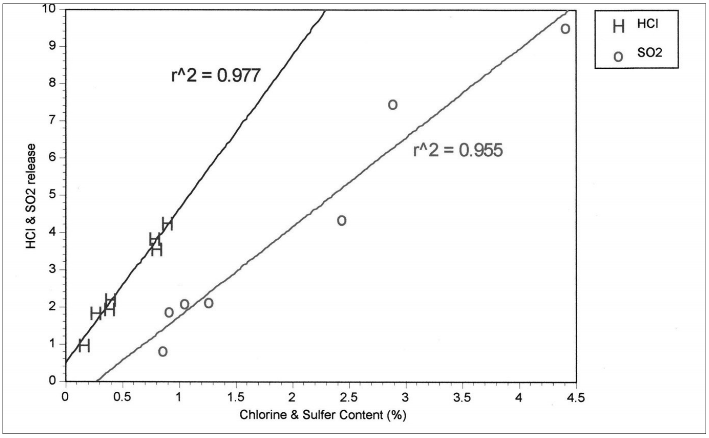

Figure 7. SO_2 and HCl Emissions as a Function of Actual Sulfur and Chlorine Content

Figure 7 shows the great precision and accuracy that TG-FTIR provides in determining the sulfur and chlorine content in coal. From Figure 8, it appears to show that HCl is evolved at lower temperatures for coals containing higher quantities of chlorine.

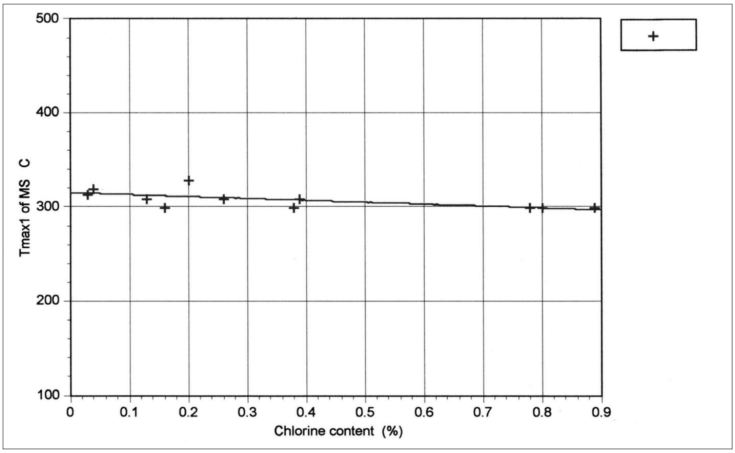

Figure 8. Maximum Temperature of HCl Release as a Function of Chlorine Content

This trend occurs as HCl becomes less bound when present in higher concentrations. The temperature maximum of the second weight loss as determined by the DTG curve and the MS curve show good correlation. The intensity ratio is the ratio of the integration of the second peak to the integration of the first peak. The curve shows that British coal has a much higher intensity ratio than that of US coal, this supports that British coal is more corrosive than US coal. The particle size of the sample affects the temperature at which the HCl is evolved. Figure 9 shows that the two peaks shown in the TG/MS curve are definitely the result of HCl existing in two different forms within the coal.

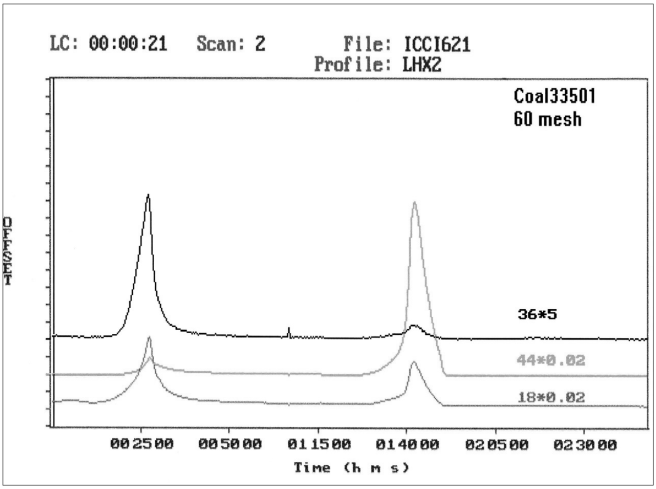

Figure 9. TG-MS of Coal

It can be concluded that the chlorine content of the coal is in good correlation with the amount of HCl evolved from the coal. Also it can be concluded that generally coals composed of smaller particle sizes evolve HCl at lower temperatures. HCl is released in three distinct regions. The first is due to HCl adsorbed on pore walls. The second represents more tightly bound HCl, and the third is the result from inorganic chlorides.

Thermal analysis can be used to determine the components of combustion products in coal. Knowing the combustion products can help improve efficiency and increase environmental awareness. At the North American Thermal Analysis Society meeting in the fall of 1989, S. A. Mikhail and A. M. Turcotte initially proposed using TGA techniques for fly ash analysis [3]. The Mikhail and Turcotte method had shortcomings including low carbon percentage determination and uncertainty associated with the decomposition mechanism of $CaSO_4$, which is used to determine the sulfur content of the fly ash. This new method refines the Mikhail and Turcotte TGA method to alleviate some of its drawbacks. Fly ash is a multi-component residue composed of carbonaceous material moisture, $CaCO_3$, $Ca(OH)_2$, $CaSO_4$, and ash. The ASTM methods are not capable of determining multiple components in fly ash simultaneously; thus, the use of ASTM methods are time consuming and tedious. There are two key differences between the new method and the Mikhail-Turcotte method [3]. The Mikhail-Turcotte method burns the carbon in air prior to decomposing the $CaCO_3$ in nitrogen. Because the carbon burns first in the Mikhail-Turcotte method, there is excess CO_2 in the atmosphere. This CO_2 can then combine with CaO to generate additional $CaCO_3$. Because the two reactions overlap, the apparent carbon percentage using the Mikhail-Turcotte method is lower than the actual percentage. The new method converts CaO into $CaCO_3$ prior to combusting the coal. This eliminates CaO from adsorbing CO_2 produced by the combustion of the coal. This is rather insignificant for analyzing bed ash as the Mikhail-Turcotte method was developed, while it is very important for analyzing carbon-rich fly ash. The second difference in the two methods is the proposed decomposition mechanism of $CaSO_4$. The new method shows a mechanism that $CaSO_4$ in a H_2 atmosphere reduces to CaS, while the Mikhail-Turcotte method has uncertainty in the decomposition mechanism. This conclusion was drawn from the TG/FTIR results shown in Figure 10.

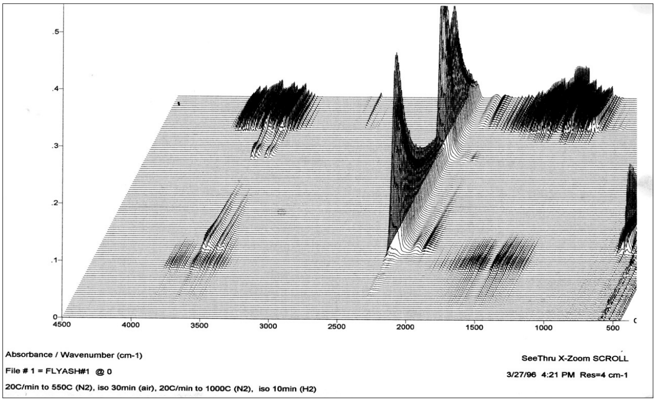

Figure 10. TG-FTIR Using New Method to Show Sulfur Reduction Mechanism

This is important because by measuring the residue of CaS, the initial sulfur content can be calculated, a limitation of the Mikhail-Turcotte method. Thermal analysis techniques provide a faster method that provides precise results as shown in Figure 11, a comparison of the TGA method results and the ASTM results.

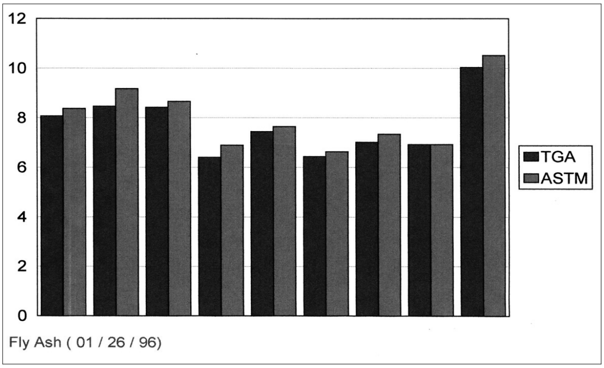

Figure 11. Comparison of Sulfur Determination By New Method and ASTM

The new method can accurately determine six components of an ash sample simultaneously.

Coal combustion occurs as a two-step process. By modeling the combustion using Arrhenius relationships and autocatalytic reaction behavior, the rate constants for different ranks of coals can be generated [4]. The kinetic constant of low-reactivity combustibles is much smaller than the high-reactivity combustibles as seen in Figures 12 and 13.

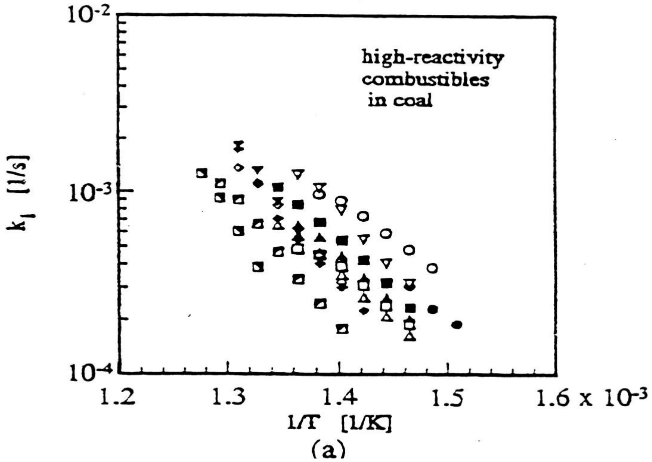

Figure 12. Kinetic Constants for High-Reactivity Combustibles

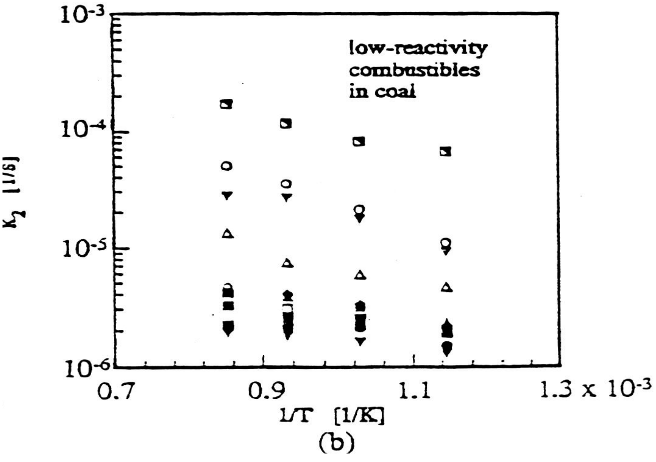

Figure 13. Kinetic Constants for Low Reactivity Combustibles

Although both the high and low-reactivity constants show temperature dependence, that of low reactivity combustibles is lower. The ignition temperature increases with decreasing volatile matter of coal as seen in Figure 14.

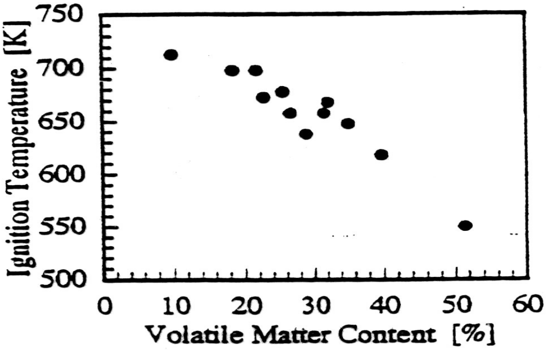

Figure 14. Ignition Temperature as a Function of Volatile Matter Content

The previous applications show how valuable TGA and evolved gas analysis are to the study of various coal systems. TGA provides a very rapid and precise method that most typically is accurate in predicting trends seen in large-scale applications providing a cheaper route for industry. It is very important that TGA's shortcomings be fully understood so the instrument is not used for applications that TGA is not capable of performing.

References

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