ANALYSIS OF ARGONNE PREMIUM COAL SAMPLES BY THERMAL METHODS

Fawzy S. Sadek and Sara A. DeBot,
Chemistry Department, Winston-Salem State University,
Martin L. King BLvd., Winston-Salem, N.C. 27110

Thermal methods are used to determine the chemical characteristics of coal as well as its reactivity. Coal grading or ranking is generally based on fixed carbon and volatiles. Percentages of moisture, volatiles, fixed carbon and ash are reported in what is referred to as proximate analysis of coal, coke or fuel materials. ASTM methods can be used to determine each of these values, however, the procedures are time consuming, results are very subjective and the most important value, fixed carbon, is not measured directly. A more reliable and faster method for conducting proximate analysis is thermogravimetry (TG) (1,2). The sample's mass is continuously measured as a function of temperature in a controlled atmosphere and fixed carbon is measured directly as well as the range of medium volatiles and ash.

Coals are further characterized according to heat values, considered by some to be one of their most important properties, especially from a commercial or industrial aspect. Gross calorific value is traditionally determined by ASTM methods which employ various bomb calorimeters (3,4). Although these methods can generate acceptable results, they are also time-consuming, can be dangerous and give only total heat values. Thermogravimetry is an equally accurate technique compared to ASTM procedures, much faster and gives more information about the sample. The calorific value of bituminous coals containing 5-40% volatile matter on dry ash free (DAF) basis can be calculated from proximate analysis data using the Goutal equation (5). Earnest and Fyans (6) developed a modified form of this equation to obtain heat values of anthracitic coals and cokes while Ferguson and Rowe (7) have presented an equation relating calorific values of lignites to their proximate analyses.

A method for calculating heat values from ultimate analysis data has been described by Culmo (8). Percents carbon, hydrogen, nitrogen and sulfur determined by elemental analysis along with TG values of moisture and ash, were used to calculate calorific values from the Dulong equation. Results were reported to be in agreement within ±3% of the ASTM values. Giazzi and Colombo introduced a modification of this equation for calculating gross and net heat values (9).

An alternative method for the direct determination of calorific values of coals by Differential Scanning Calorimetry (DSC) was introduced by Fyans in 1977 (10). This technique measures heat flow as a function of programmable temperature with the total area under the curve being proportional to the heat of combustion. A typical thermocurve for coal shows a two step decomposition with the first peak being the combustion of volatiles and the second relates to fixed carbon. Fyans and

Earnest have reported surprisingly good agreement between the area of the DSC peaks and the ASTM calorific values (10-12).

In recent years the goals of thermal analysis investigations have become more and more quantitative. Unresolved problems associated with DSC, however, have brought results by this method under question. Varhegyi, et.al. (13), showed that DSC curves reveal considerably less energy release than the true reaction heats of oxidation of organic materials and the measured heat is strongly affected by the experimental conditions. To correctly characterize calorific values for volatiles produced in various steps of thermal decomposition as well as the heat of oxidation of the resulting char, they proposed the use of catalysts as aids to combustion at the low temperatures of DSC. In an effort to improve the DSC technique for coal analysis, we have focused on the use of metal oxides as well as the effects of variables related to sample characteristics. Heat values determined by DSC and bomb calorimeters are compared with calculated values from proximate and ultimate analysis.

EXPERIMENTAL SECTION

Apparatus:

Ultimate Analysis of coals by the determination of C/H/N/S was made on the left channel (O/S) of a Carlo Erba Elemental Analyzer Model 1106. A model C-31 Cahn Co. microbalance and IBM computer were interfaced with the instrument. Eager 100 software of Carlo Erba was used for operating the system and data analysis.

The Mettler system used for proximate analysis and drying of coal samples was composed of a TG-50 thermogravimetric unit, M3 microbalance, TC-10A controller TA processor equipped with TA 3000 version 3.1 software attached to an IBM/PC computer for data storage, TA-70 for data processing, RO-80 Swiss printer/plotter for actual time thermocurve printing and Epson HI-80 for printing processed data. A Mettler DSC 20 with measuring cells containing medium sensitivity sensors was used to determine heat values of coal samples directly. Nitrogen used for pyrolysis was purified with a Supelco High Capacity Heated Carrier Gas Purifier, cat.# 2-3802.

Samples and Materials:

The 100 mesh Premium Coal Samples used in this study were supplied by Argonne National Laboratory (ANL). All chemicals used for filling reactors, and consumables for Elemental Analysis were purchased from Carlo Erba Co.. Platinum crucibles with fine platinum mesh lids were used for proximate analysis of coal. Standard 40 μl aluminum or gold crucibles were utilized in the determination of heat values by DSC. Two equal weight crucibles with lids were selected and a hole of approximately 0.5mm was made in the center of each lid. A 1:1 mole ratio mixture of

magnesium oxide and silver oxide was finely ground in a mortar and stored in a vial shell in a vacuum dessicator until use. Approximately 0.3 to 0.6 mg dried coal was spread evenly in the center of the crucible and from 8 to 12 mg of the additive mixture was placed over the sample. The heat capacity was counterbalanced by putting an amount of the spent additive in the reference crucible equal to 93% of the freshly prepared mixture.

Ultra high purity (99.99% or better) oxygen, nitrogen, helium and argon were purchased from National Specialty Gases, a division of National Welders Supply. Magnesium oxide, lead chromate (Analytical Reagent, Mallinckrodt), silver oxide (Baker and Adamson), praeseodymium oxide (Alpha Inorganics), calcium oxide, copper oxide (certified ACS, Fisher), and lead dioxide (Fisher) were used as received.

Procedures:

Remixing of coal samples was done according to recommendations of the supplier before the ampoules were opened in a glove box filled with argon gas. Approximately 25 mg of the as received coal was placed in a platinum crucible in the TGA furnace in dry, oxygen free nitrogen for moisture analysis. The temperature was brought to 112°C at a heating rate of 100 °C/min and then held isothermally for 2 min. The evaporation of moisture from each of the seven samples is graphically presented in Fig. 1.

Proximate and ultimate analyses were made on the dried coal samples. Percent moisture and ash were used for calculating results on dry basis as well as moisture and ash free basis (14). Heat values were calculated from proximate analysis data applying the Goutal equation and using in house software. The software calculates the Heat Value (ΔH) as follows: ΔH (cal/gram) = 82C + aV, where C is % fixed carbon, V is % volatiles and "a" is the Goutal coefficient. The value of "a" is a function of V and is obtained by interpolating known values of "a" at various values of V as derived by Goutal. Elemental analysis percentages were used in the calculation of heat values from the modified Dulong equation (8). Gross and net heat values are printed at the end of each analysis in calorie/gram units. These are changed to BTU/lb for comparison with ASTM bomb calorimeter values.

A procedure for determining heat values by DSC was stored on the TC-10A processor. This included 10°C/min heating rate from room temperature to 600°C. An oxygen flowrate of 20 ml/min was used. Integration of the heat flow during the dynamic experiment gives the heat change in coal directly. The two peak curve was integrated over a baseline starting at 105°C to the end of the run.

RESULTS AND DISCUSSION

Proximate and ultimate analyses of seven bituminous Premium Coal Samples are shown in Table 1. The calculated precentages are

comparable with those reported by ANL. Proximate analysis data made by TG were calculated by the instrument while data listed for ANL/ASTM were derived indirectly from the values of volatiles and ash provided with the samples. ASTM criteria for proximate analysis precision in reproducibility of data between two laboratories or by different methods are met with minor exceptions found in volatile matter of the Illinois #6 sample and percent ash of the Wyodak sample.

In ultimate analysis (14) the four major elements of coal were determined simultaneously on 1.0 to 3.0 milligram samples (Fig.3). The ANL data were made on different aliquot portions. Results are comparable with the exception of Illinois #6 and Blind Canyon carbon percentages and Upper Freeport hydrogen values. The sulfur values show a distinct difference for Illinois #6. In both proximate and ultimate analysis three or four values are compared with each other or with their counterpart made by a standard method. The logical way to compare sample data is to simplify to one numerical value. Mathematical equations to combine each group of data have existed for several decades. Goutal introduced his equation to give the heat value of bituminous coals as a function of percent volatiles and fixed carbon. By applying this equation to calculate heat values of TG data as well as ANL data we arrived at the values shown in Table 1. The average error of the TG heat values relative to ANL data calculated with the same equation is 3.9%. The difference between TG data and bomb calorimeter values is 3.5%. It is worth mentioning that most TG calculated heat values are slightly higher than those determined by the ASTM/bomb calorimeter method. This phenomenon repeats itself with calculated heat values from elemental analysis results. Work with elemental analysis confirmed that a catalyst is needed to insure the complete combustion of carbon in organic compounds regardless to the use of large amounts of oxygen and high temperatures. Oxides of copper, chromium, tungsten, vanadium and others (14) have been used at temperatures up to 1050 ºC to accomplish the complete oxidation of carbon to carbon dioxide. A comparison of elemental analysis results with those obtained with bomb calorimeters shows an average error of about 1.5% higher which may indicate a more complete combustion of the sample.

Direct determination of heat values by DSC traditionally has produced results 20 to 40 percent lower than those determined by bomb calorimeters. Varhegyl, et. al., proved by mass spectrometry that these low results are due to the formation of carbon monoxide (13). A mixture of cupric oxide and lead chromate was used as a catalyst but the true heat of combustion of the coal samples was not achieved even though the instruments maximum temperature reaches 750 ºC. Many commercially available DSC instruments have a maximum of only 600 ºC and some manufacturers recommend pressurized containers made of either glass or stainless steel and/or pressurized DSC cells, further complicating the situation. It was found that the effects of factors such as heating rate, sample mass and particle size, type and amount of additive, hole size in container lid as well as

oxygen flowrate, are dependent on each other.

Heating metal oxides in an oxygen atmosphere using TG proved that most of the oxides are stable and usually contain the metals in the highest oxidation state (16). Contrary to this statement the TG curves of calcium, magnesium, lead, praeseodymium and silver oxides in Fig. 4 show a mass loss. The curves were obtained in an atmosphere of oxygen and at a heating rate of 40 C/min. Dissociation of these oxides with the release of active oxygen appears to be definite. Magnesium oxide and silver oxide release oxygen and dissociate without phase transitions while calcium oxide and praeseodymium oxide dissociate with phase transitions. Lead dioxide loses oxygen as shown in Fig. 4 in two steps below 650 °C and a third step above 650 °C which disturbs the DSC curve in that region.

Magnesium oxide (Fig. 5) was selected as a combustion aid due to its release of oxygen in the region of coal volatile matter to assist in its complete oxidation. In addition, it has been reported that magnesium oxide catalyses the oxidation of carbon monoxide to carbon dioxide (17). Formation of carbon dioxide releases approximately four times the amount of heat as the formation of carbon monoxide from the same amount of carbon. This is basically the reason for the lower heat values measured in unpressurized low temperature DSC. Silver oxide (Fig.5) releases its oxygen relative to the fixed carbon combustion region as shown in Fig. 6. Heat value results determined using the magnesium-silver oxide mixture are listed in Table 1. DSC results are comparable with ASTM values.

CONCLUSIONS

Thermogravimetric and elemental analysis data have been used to derive heat values of Argonne Bituminous Premium Coal Samples. The average error between heat values calculated from proximate analysis data by the classical Goutal Equation and ASTM/bomb calorimeter values was less than 4%. It was found to be less than 2.0% between Ultimate Analysis values calculated by the Dulong Equation. A comparison of heat values obtained directly by conventional low temperature DSC using metal oxide additives shows an average error of 0.5%.

ACKNOWLEDGMENT

LITERATURE CITED

(1) Sadek, F.S.; Herrell, A.Y. Thermochimica Acta, 81 (1984) 297.

(2) Ottaway, M., Fuel 61 (1982) 713.

(3) "ASTM Designation D2015-85, Annual Book of ASTM Standards, 05.21 (1985).

(4) "ASTM Designation D3286-85, Annual Book of ASTM Standards, 05.21 (1985).

(5) Goutal, M. Compt. Rend., 135 (1902) 477.

(6) Earnest, C.M.; Fyans, R.L. Thermal Analysis Applications Study #21, Perkin-Elmer Corp., Norwalk, CT (1977).

(7) Ferguson, J.A.; Rowe, M.W. Thermochimica Acta, 107 (1986) 291.

(8) Culmo, R.F., Elemental analysis Application Study #2, Perkin-Elmer Corp., Norwalk, CT (1977).

(9) Giazzi, G.; Colombo, B. The Journal of Coal Quality, 2 (1982) 26.

(10) Fyans, R.L., Thermal Analysis Application Study #21, Perkin-Elmer Corp., Norwalk, CT, (1977).

(11) Earnest, C.M., "Analytical Calorimetry" (Johnson, J.F.; Gill, P.S.Eds.) Vol. 5, Plenum Press, New York, (1984), 343.

(12) Earnest, C.M. Int. Instrum. Res., (1985), 57.

(13) Varhegyi, G; Szabo, P.; Till, F. Thermochimica Acta, 106 (1986) 191.

(14) Sadek, F.S.; deBot, S.A. "Rapid Automated Methods For Coal Ultimate Analysis" Proceedings of the 6th International Coal Testing Conference, (1987) 97.

(15) "ASTM Designation D3180, Annual Book of ASTM Standards, Vol. 05.05 (1984).

(16) Wendlandt, W.W. " Thermal Analysis" 3rd Edition John Wiley & Sons, New York (1986) 179.

(17) Lundsford, J.H.; Jayne,J.P. Journal of Chemical Physics, 44 (1966) 1492.

Table 1. COMPARISON OF ARGONNE PREMIUM COAL SAMPLE DATA OBTAINED
BY DIFFERENT THERMAL METHODS.

PROXIMATE ANALYSIS*

	TGA (%)			ANL/ASTM (%)		
	Ash	VM	FC	Ash	VM	FC
1. Upper Freeport	13.2	27.6	59.2	13.2	27.5	59.3
2. Wyodak	7.5	45.2	47.3	8.8	44.7	46.5
3. Illinois #6	15.4	36.6	48.0	15.5	40.1	44.4
4. Pittsburgh #8	9.2	36.7	54.1	9.3	37.8	52.9
5. Pocahontas #3	4.3	19.0	76.7	4.8	18.6	76.6
6. Blind Canyon	4.6	45.2	50.2	4.7	45.8	49.5
7. Lewis Stockton	20.0	30.2	49.8	19.8	30.2	50.0

ULTIMATE ANALYSIS*

	ELEMENTAL ANALYSIS (%)				ANL/ASTM (%)			
	C	H	N	S	C	H	N	S
1. Upper Freeport	75.1	4.6	1.5	2.3	74.2	4.1	1.4	2.3
2. Wyodak	67.9	4.9	1.0	0.8	68.4	4.9	1.0	0.6
3. Illinois #6	64.6	4.5	1.2	4.5	65.7	4.2	1.2	4.8
4. Pittsburgh #8	75.0	5.0	1.5	2.4	75.5	4.8	1.5	2.2
5. Pocahontas #3	85.7	4.4	1.2	0.7	86.7	4.2	1.3	0.7
6. Blind Canyon	74.9	5.6	1.5	0.8	76.9	5.5	1.3	0.6
7. Lewis Stockton	66.3	4.3	1.2	0.8	66.2	4.2	1.3	0.7

HEAT VALUES* (BTU/lb)

	CALC. TGA	GOUTAL ANL	CALC. E. A.	DULONG ANL	DIRECT DSC	ANL/ASTM
1. Upper Freeport	13535	13537	13701	12874	13611	13467
2. Wyodak	11687	11487	11578	11641	11800	11717
3. Illinois #6	11817	10982	11664	11363	11951	11951
4. Pittsburgh #8	13200	14356	13684	13415	13740	13629
5. Pocahontas #3	16090	14867	15141	15102	15029	15024
6. Blind Canyon	12417	12240	13633	13743	13896	13925
7. Lewis Stockton	12005	12057	11869	11626	11857	11810

* As received, on dry basis.

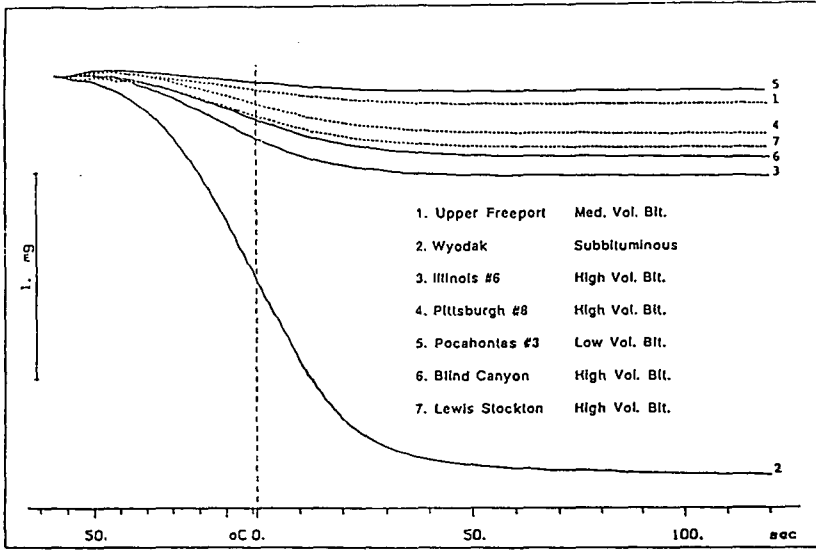Figure 1. Drying of ANL Premium Coal Samples by TGA.

1. Upper Freeport	Med. Vol. Bit.
2. Wyodak	Subbituminous
3. Illinois #6	High Vol. Bit.
4. Pittsburgh #8	High Vol. Bit.
5. Pocahontas #3	Low Vol. Bit.
6. Blind Canyon	High Vol. Bit.
7. Lewis Stockton	High Vol. Bit.

Figure 2. Proximate Analysis of ANL Bituminous Coal on Dry Basis.

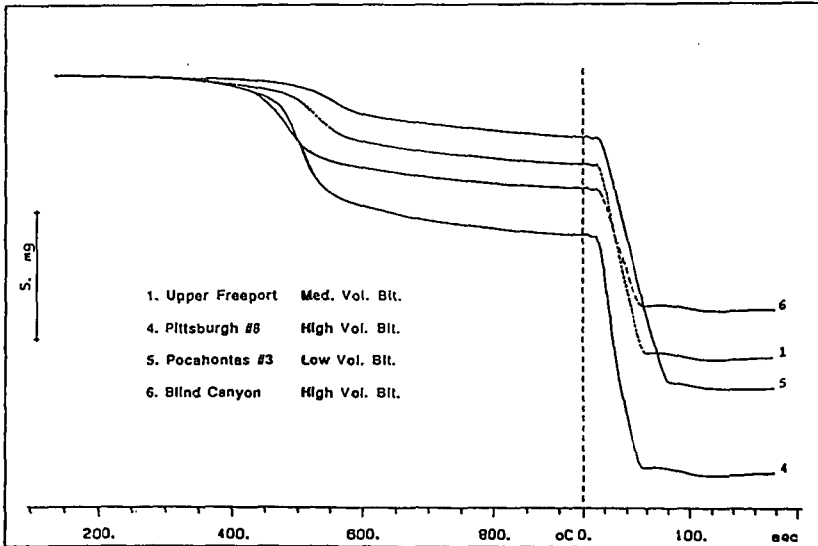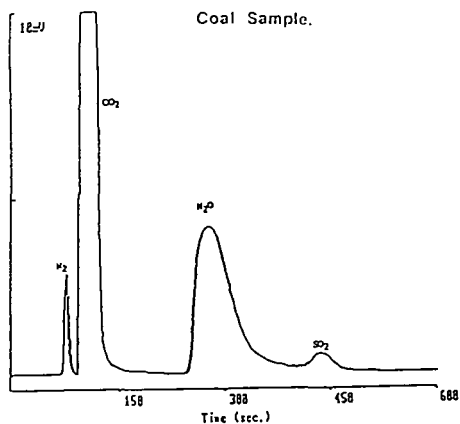| 1. Upper Freeport | Med. Vol. Bit. |
4. Pittsburgh #8	High Vol. Bit.
5. Pocahontas #3	Low Vol. Bit.
6. Blind Canyon	High Vol. Bit.

45

Figure 3. Elemental Analysis of Upper Freeport
Coal Sample.

Date   : 02-13-1794   Time : 09:37:15   Company name : WSSU
Sample : 168   COAL 11 AS 15 100 K   Type : Unknown
Sample   Weight   : 1.8972   Base Line drift (calcVt): 12
Operator : AXX

I	Ret.T.	Area (calcVts)	Area %	Comp. %	Peak name
1	77	16390	1.05	1.771672	Nitrogen
2	97	1287850	82.552	73.47242	Carbon
3	276	239704	15.365	4.764939	Hydrogen
4	636	16092	1.031	1.971164	Sulphur

Carb./Hyd. Area =   5.372660   Carb./Nitr.Area =   78.57535
Carb./Sulp.Area =   80.05542
E. R. V. = 7871.641   R. R. V. = 7627.598
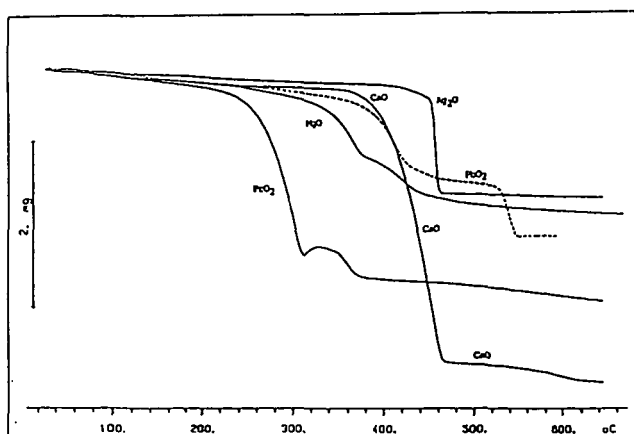
Figure 4. Thermocurves of Five Metal Oxides.

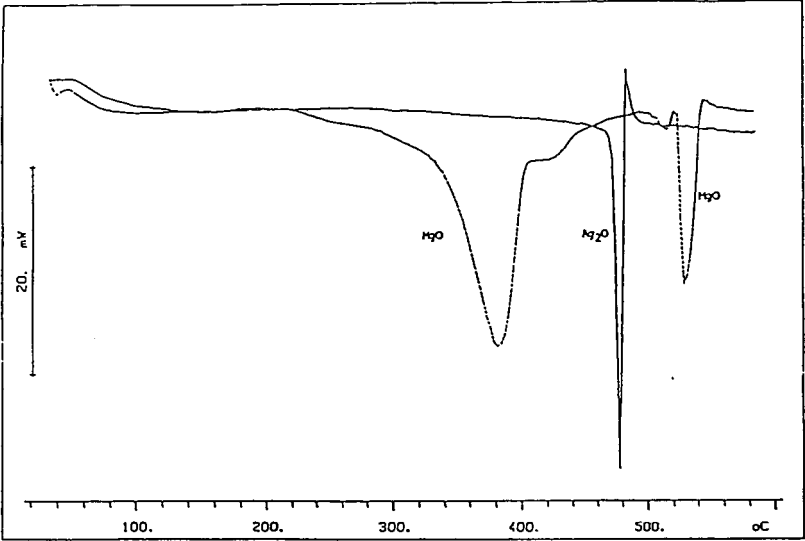Figure 5. DSC of Magnesium Oxide and Silver Oxide.

Figure 6. DSC Curves of Pittsburgh #8 Coal Sample at 10°C / min.