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## Heat Content of Coal by Pressure DSC

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### ABSTRACT

The heat of combustion of coals is determined by pressure DSC using standard thermal analysis procedures. The experimental heat of combustion is corrected by calibration using the heat of combustion of a reference material. The method is applied to several coal samples that have also been analyzed by bomb calorimetry.

### INTRODUCTION

Heat content, or heat of combustion, is an important quality control parameter for coal. It is used along with the fixed carbon content of the coal in classifying the coal by rank (1) according to its degree of progression in the natural coalification process from lignite to anthracite. Hence, it is important to both the suppliers and users of coal to have a rapid, accurate, and reliable method for determining the heat content of coal.

The most widely used methods for determining coal heat content are the ASTM accepted adiabatic (2) and isothermal jacket (3) bomb calorimeters. However, these methods suffer from the disadvantages of being time consuming and requiring fairly complicated operator technique. Thermal analysis techniques, particularly differential scanning calorimetry (DSC), offer a viable alternative to the ASTM methods.

Several studies (4,5,6) have been made attempting to correlate various parameters of differential thermal analysis (DTA) peaks with the heat content of coals. While most of these studies were at least moderately successful, they are not applicable as quality control techniques due to the time and operator expertise required. More importantly, none of the DTA studies were quantitative and hence could not be used as a direct measure of the heat content. DSC, however, does provide the ability to quantify heats of reaction, and enables the user to directly determine the heat content of coal. The TA Instruments Pressure DSC (PDSC), which is usable to 7 MPa (1000 psig), is particularly amenable to such determinations since the increased pressure of the reactive gas permits determination of the heat content of most coals in 20 minutes.

### EXPERIMENTAL

The pressure DSC cell is available as an accessory to the Q1000 DSC or as a stand-alone analyzer. It provides heat flow measurements from ambient temperature to 725 °C under pressures of 1 Pa to 7 MPa (0.01 torr to 1000 psi). The cell includes pressure control valving, pressure gauge and over-pressure protection. It uses standard DSC technology and the single-term heat flow equation.

## PROCEDURE

A 1.0 to 1.5 mg test specimen is placed into a tared hermetic aluminum sample pan with a pinhole in the lid and weighed. The weighed sample is then sealed and placed in the PDSC cell at ambient temperature and pressure. An empty capsule of similar type and weight is placed on the reference position of the PDSC. The cell is closed and prepared for pressurization.

The cell is purged by pressurizing to 350 kPa gauge pressure (50 psig) with the reactive gas (O<sub>2</sub>). The gas is then discharged by gradually opening the coarse exit valve. The cell is again pressurized to 350 kPa gauge pressure (50 psig) and a flow of 50 mL/min is maintained through the cell for 30 seconds. With both exit ports closed, the cell is pressurized to 3.5 MPa gauge pressure (500 psig) with O<sub>2</sub>.

Initiate a 20 °C/min heating rate from 150 to 600 °C. If the exothermic combustion is complete at 600 °C (that is, the heat flow signal has returned to the baseline) the experiment is terminated. However, if the combustion is still proceeding, the experiment continues with a 15-minute isothermal segment until combustion is complete. A typical scan is shown in Figure 1. The area under the combustion exotherm is measured using the Q DSC peak area calculation software. Peak Area Calculation.

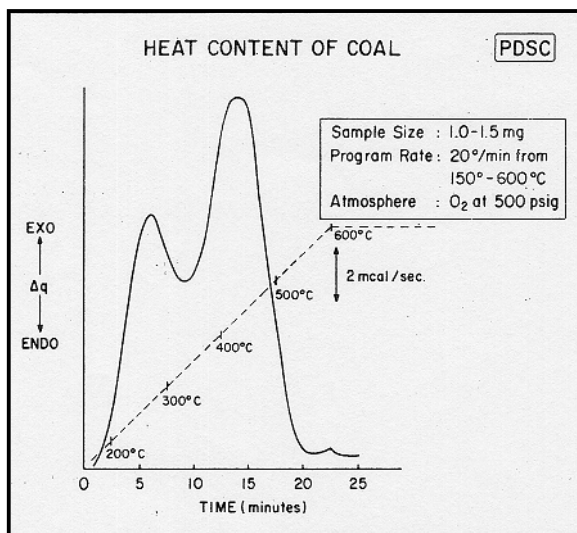


Figure 1- PDSC Combustion of Coal

## CALCULATIONS

The corrected heat of combustion is obtained from the mass normalized energy times a calibration factor. The calibration factor is obtained by performing the same analysis on a material of known calorific value:

$$\begin{aligned}\Delta H_C &= \Delta H_{(PEAK)} * E_- \\ &= \Delta H_{(PEAK)} * \Delta H_{(StdRef)} / \Delta H_{(StdMeas)}\end{aligned}$$

Where:

- $\Delta H_C$  = Corrected heat of combustion (W/g)  
 $\Delta H_{(PEAK)}$  = Measured heat (W/g)  
 $E_{-}$  = Calibration factor (dimensionless)  
 $\Delta H_{(StdRef)}$  = Reference value for mass normalized heat of combustion of reference material (W/g)  
 $\Delta H_{(StdMeas)}$  = Heat of combustion for reference material (W/g)

## DISCUSSION

PDSC data obtained using the above procedure and the ASTM adiabatic bomb calorimeter data on a series of coal samples are shown in Table 1. The average deviation for the PDSC procedure is 3 %, or less, provided that small samples (< 2 mg) are used.

Coal Sample	HEAT CONTENT OF COAL CALORIFIC VALUE (kW/g)		PDSC
	Adiabatic		Avg. Deviation % (rel.)
	Bomb Calorimeter	PDSC	
Bituminous	33.95	34.09	2.1
Bituminous	34.11	34.10	2.5
Bituminous	35.20	35.97	2.5
Bituminous	35.42	35.75	0.9
Bituminous	35.53	35.41	1.6
Bituminous	33.65	34.61	2.9
Sub-bituminous	25.25	25.70	2.1
Lignite	15.21	15.51	2.2

Table 1

The adiabatic bomb calorimeter values are gross calorific values, while the PDSC values are corrected gross calorific values. This distinction is necessary since some of the products formed by combustion in the bomb calorimeter method are recovered, while those formed by the PDSC method are all converted to gases. Hence, heats of vaporization and thermal emissivity must be considered in the PDSC results. The PDSC calibration coefficient, E', combines these effects into a correction constant, provided a suitable standard material is used. 2,3 Benzantracene is a suitable standard for coal, since it has a known heat of combustion (calculated from NBS Circular 500) (7) and approximately the same hydrogen content as most coals. Benzoic acid, which is normally used as the standard material in the bomb calorimeter method, is not used here because it melts prior to combustion and some vaporization losses occur. The E' value should be in the range 1.0 - 1.25. The PDSC values are not corrected for the nitrogen and sulfur content of the coal. Ignoring the contributions of these substituents saves time and

operator effort without any appreciable loss in accuracy, since in most cases, the corrections for nitrogen and sulfur would only affect the combustion heats obtained by < 0.5 %. Both the bomb calorimeter and PDSC values listed in Table 1 are corrected for moisture and ash. (The results are listed in kW/g. Multiply by 430 to convert to BTU/lb.)

Since coal samples oxidize on standing and change in composition, it is important that they be analyzed as soon as possible after the gross sample is collected. The elapsed time between sampling and analysis should not exceed 30 days, if the heat content is an important quality control parameter.

## REFERENCES

1. D 388, Method D, "Classification of Coals by Rank", ASTM International, West Conshohocken, PA.
2. D 2015, "Gross Calorific Value of Coal and Coke by the Sole-Heated Oven", ASTM International, West Conshohocken, PA.
3. D 5865, "Gross Calorific Value of Coal and Coke", ASTM International, West Conshohocken, PA.
4. C. M. Gamel and W. J. Smothers, *Analytica Chimica Acta*, **1952**, 6, pp. 442 - 449.
5. J. B. Stott, O. J. Baker, *Fuel, (London)*, 32, **1953**, 32, pp. 415 - 427.
6. R. W. Grimshaw, A. L. Roberts, "Differential Thermal Investigations of Clays", *Mineralogical Society (London)*, **1957**, pp. 404 - 417.
7. "Selected values of Chemical Thermodynamic Properties", Nat. Bur. Standards (US) Circ. No. 500, (**1952**)

## KEY WORDS

enthalpy, minerals, pressure differential scanning calorimetry

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