DSC determination of coal specific energy

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Abstract

The specific energy of several types of Australian coal was determined directly by DSC, using a standard coal as calibrant. By subdivision of the combustion profile into separate peaks representing combustion of volatile matter and residual char, the specific energies of these components were also determined

INTRODUCTION

Specific energy (heat of combustion) is one of the most important quality control parameters of coal. For the industrial combustion of coal in the production of electrical energy, estimates of the overall efficiency of the process are based on the coal specific energy parameter. This parameter is also used in the classification of coals of rank lower than medium-volatile bituminous [1].

The standard method for the determination of coal specific energy is by adiabatic oxygen bomb calorimetry [2], which provides very accurate data but is time-consuming and requires specialist operator techniques [3,4]. Two alternative methods have been suggested: the calculation of specific energy from proximate and ultimate analyses data [4–8] and the direct determination of specific energy by DSC [3,9–15]. The DSC method provides rapid and reproducible coal specific energy data.

EXPERIMENTAL

The coal samples investigated included three brown coals and two bituminous coal maceral concentrates. A standard reference coal, ASCRM-009, certified by the Standards Association of Australia, with known specific energy, was used as a standard to calibrate the DSC instrument. The

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Sample	Proximate (%d	lb) ª			Ultimat	c (Ldmf)	q			$Q_{\rm g}$ dry
(air dried)	M° (%ar) ^d	Ash	∘ MV	FC ¹	 ပ	Н	z	S	0	$(MJ kg^{-1})$
Reference coal	1.1 (%db)	95	20.2	70.3	80.4	4.3	1.5	0 35	13.5	32.32
Morwell coal	12.7	3.8	47.7	48.5	69 8	4.8	0 55	0.27	24.6	26.21
Gelliondale coal	73	5.4	49 0	44.7	665	4.7	0.56	0.78	27.5	25.99
Loy Yang coal	15 6	1.1	51.7	47.2	68.2	4.9	0 57	0.32	26.0	26.16
Bullı vitnnıte	1.6	13 6	22.3	76 3	88.4	5.3	2.0	0.3	4.0	35.70
Liddell vitrinite	6.3	14	35.2	63.4	81.8	5.5	2.1	0.4	10.2	33.70

TABLE 1

^a db, dry basis ^b dmif, dry mineral and inorganic free. ^c M, moisture ^d ar, as received. ^e VM, volatile matter. ^f FC, fixed carbon

TABLE 2

The	DSC	instrument	constant	based	on	tın	metal	standard	

Melting point (°C)	T _{onset} (°C)	$\frac{\Delta H_{\rm fus}}{(\rm kJ~g^{-1})}$	$\frac{A/M}{(\text{kJ g}^{-1})}$	k	k _{av}
231 9 ª	233 2	60.61 ª	59.68	1 016	
231 9 ª	233.5	60.61 ^a	59 72	1.015	1.015 ± 0.001

^a From ref 16

proximate and ultimate analyses data for the samples investigated are given in Table 1.

The DSC results of coal combustion were obtained using a Perkin-Elmer DSC 7 system, which is based on the power compensation principle. The following experimental conditions were used: scanning rate, $20 \,^{\circ}$ C min⁻¹; sample mass, 1–1.5 mg; crucible type, platinum; atmosphere, dry oxygen; flow rate, $20 \,\text{ml} \times \min^{-1}$.

RESULTS AND DISCUSSION

The relationship between DSC peak area and specific energy of coal can be expressed as

$$Q_{g}(MJ kg^{-1}) = kA/M(kJ g^{-1})$$
⁽¹⁾

where Q_g is the specific energy, A/M is the normalized DSC area and k is the instrument constant.

The DSC system was initially calibrated using tin metal as standard. The results are given in Table 2. The instrument constant based on this standard is $k_{\rm sn} = 1.015 \pm 0.001$. Subsequently, a reference coal was employed as a standard. The DSC curve of the reference coal is shown in Fig. 1 and the corresponding data are given in Table 3. The instrument constant obtained was $k_{\rm ref} = 1.191 \pm 0.011$. A k value greater than unity may be explained by the fact that the gross heat released in the combustion process is incompletely determined in the DSC cell, owing to partial radiative release to the cell environment. The instrument constants based on tin metal and the reference coal are clearly different. Because metal fusion and coal combustion are different thermal processes, the instrument constant based on tin metal fusion is unsuitable for the determination of coal specific energy and hence for this purpose the instrument constant based on the reference coal was used.

The DSC data for the combustion of several coals are listed in Table 4. A linear correlation exists between the DSC peak area and the coal specific energy. As the samples investigated included coals of different rank, it is apparent that the relationship between DSC peak area and coal specific



Fig 1 DSC combustion curve of a reference coal.

TABLE 3

The DSC instrument constant based on the combustion of a reference coal (Perkin-Elmer DSC 7 system)

	Run 1	Run 2	Run 3	
$\overline{Q_{g,\text{bomb}}(\text{MJ kg}^{-1})}$	32.32	32.32	32 32	
A/M (kJ g ⁻¹)	27.35	26.85	27 21	
k	1.182	1.204	1 188	
k _{av}	1.191 ± 0.011			

TABLE 4

Sample	$Q_{g,bomb}$ (MJ kg ⁻¹)	$\frac{A/M}{(kJ g^{-1})}$	$Q_{g,DSC}$ (MJ kg ⁻¹)	DQ_g^a (MJ kg ⁻¹)	Error (%)
Reference coal	32.32	26.85	31.98	0.34	1.04
Morwell	26 21	21 43	25.52	0 69	2.63
Gelliondale	25.99	21.29	25.35	0.64	2.45
Lov Yang	26.16	21.49	25.60	0 57	2.16
Bulli vitrinite	35.70	30.73	36.61	-0.91	-2.54
Liddell vitrinite	33.70	27 93	33.27	0.43	1.28

 $\overline{^{a} DQ_{g} = Q_{g,bomb} - Q_{g,DSC}}$

Sample	A_1/A_2	Q ₁ (MJ kg ⁻¹)	Q_2 (MJ kg ⁻¹)	VM/FC					
Reference coal	0.173	4.72	27.27	0.287					
Morwell	0.516	8.68	16.84	0.984					
Gelliondale	0.561	9.12	16.24	1.116					
Loy Yang	0.559	9.18	16.42	1 095					
Liddell vitrinite	0.229	6.20	27.07	0 555					
Bulli vitrinite	0.132	4.27	32.34	0 292					

TABLE 5

DSC	data	for	the	com	bustion	of	coal	s

energy is independent of coal rank, which verifies that it is not inconsistent to use a high rank coal as a DSC standard in the determination of brown coal specific energy. From Table 4, the specific energy as determined by DSC is in good agreement with that derived by bomb calorimetry to within 3% or less.

The DSC combustion profile (Fig. 1) reveals two or more sequential exothermic peaks for coal combustion, which are assigned to the combustion of volatile matter and residual char respectively. Hence DSC provides information on the coal combustion process and it is possible to determine the individual combustion enthalpies of the volatile matter and residual char from DSC profiles [14].

Since specific energy is proportional to DSC peak area, the ratio of DSC peak areas for the combustion of volatile matter (A_1) and residual char (A_2) is equivalent to the ratio of the specific energies of volatile matter, Q_{g1} , and residual char, Q_{g2} . The peaks corresponding to the combustion of volatile matter and residual char are partially overlapped. Areas A_1 and A_2 were therefore sub-divided by a straight line perpendicular to the baseline through the minimum of the two peaks, as shown in Fig. 1. This method has been recommended by Chiu [17]. The ratio A_1/A_2 and the values for Q_{g1} and Q_{g2} ,



Fig. 2 Relationship between volatile matter specific energy and volatile matter content.



Fig. 3 Relationship between residual char specific energy and fixed carbon content.

as calculated by the following equations, are given in Table 5:

$$A_1/A_2 = Q_{\rm gl}/Q_{\rm g2} \tag{2}$$

and

$$Q_{\rm g} = Q_{\rm g1} + Q_{\rm g2} \tag{3}$$

A relationship between Q_{g1} and the volatile matter (VM) content of coal was found, as shown in Fig. 2, and is expressed as

$$Q_{g1}(MJ kg^{-1}) = 0.158(VM)(\% dry basis) + 1.05$$
 (r = 0.989) (4)

A similar relationship was found between Q_{g2} and the fixed carbon (FC) content of coal, as shown in Fig. 3, and is expressed as

$$Q_{g2}(MJ kg^{-1}) = 0.518(FC)(\% dry basis) - 7.58$$
 (r = 0.986) (5)

Consequently, a relationship exists between Q_{g1}/Q_{g2} and (VM)/(FC): $Q_{g1}/Q_{g2} = 0.517(VM)(FC) - 0.012$ (r = 0.990) (6)

Thus it is apparent from the present study that DSC provides a convenient, rapid and reproducible method for the determination of coal specific energy and the individual volatile matter and residual char specific energies. However, in order that such derived data are of comparable accuracy to that derived by bomb calorimetry, it is essential to use a standard coal for DSC calibration.

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