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CALORIFIC VALUE OF LIGNITES FROM PROXIMATE ANALYSIS

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ABSTRACT

An equation relating the calorific values of lignites to their proximate analyses (% moisture, % ash, % volatile matter, and % fixed carbon) is presented. Equations based on proximate analysis have been developed for higher ranks of coal, but not for lignite.

Our equation was determined by least squares fitting using matrix algebra. Gauss reduction was used to solve the simultaneous equations. Proximate analysis data and calorific values for 23 lignites were obtained from the Pennsylvania State University Coal Research Laboratory's Coal Data Bank. The best fit equation gave an average deviation of $\pm 1.2\%$ from bomb calorimetry measurements of the calorific value for these 23 lignite samples. Considering the broad-based definition of the values reported in proximate analysis, this represents good agreement with the measured values.

INTRODUCTION

One of the more important properties of coal from a commercial standpoint is its calorific or heating value, i.e., the heat produced upon burning. The heating value can be obtained accurately by bomb calorimetry, which is, however, time consuming and requires an experienced technician to obtain reliable results. For higher ranked coals (sub-bituminous and higher grades), equations are available that relate calorific value to ultimate analysis, i.e., measurement of ash, carbon, hydrogen, nitrogen, sulfur, chlorine, and oxygen contents [1]. Although such equations yield calorific value with suitable accuracy, on the same order as bomb calorimetry, ultimate analysis is also time- and labor-intensive and uses expensive equipment. Finally calorific values for the higher ranked coals can also be obtained from proximate analysis data [2,3]. However, no equation has been reported previously for lignites. Such an equation would be very useful since proximate analysis is a standard method for analyzing coals. It would be especially valuable now that a quick and reliable procedure for conducting proximate analysis is available, i.e., thermogravimetry (TG) [4–13]. TG is a viable alternative, and an equally accurate technique compared to the ASTM procedures [14], which are cumbersome, labor intensive and time consuming. Proximate

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analysis by TG takes ~ 30 min. Construction of an inexpensive thermobalance which is interfaced to an Apple II + microcomputer has been proposed by Ferguson et al. [15].

It is the purpose of this paper to describe our development of an empirical equation which relates the heating value of lignites to their proximate analysis. An average standard deviation of only $\pm 1.2\%$ was obtained between our calculated values and the measured calorific values corrected to a dry, ash-free basis listed for 23 lignites by the Pennsylvania State University Coal Research Laboratory.

EXPERIMENTAL APPROACH

We utilized matrix algebra [16,17] to obtain a least squares best fit for an equation to relate calorific value to the parameters of proximate analysis, i.e., % moisture (M), % ash (A), % volatile matter (VM), and % fixed carbon (FC). Proximate analysis and calorific value data were provided by the Pennsylvania State University Coal Research Laboratory for 23 lignite A samples; therefore, in the following calculations, $i = 1$ to 23.

Matrices allow the derivation of a simple expression for the least squares estimates of parameters in a general linear form.

$$y = C_0 + C_1 x_1 + C_2 x_2 + \ldots + C_k x_k + \epsilon \tag{1}$$

This expression relates a response, y, to a set of k independent variables, $x_1, \ldots, x_k$, the error, ϵ, and the constants, $C_0, C_1, \ldots, C_k$. If a sample of n $(n > k)$ measurements are taken, given n sets of the independent variables, $x_1, \ldots, x_k$, the ith individual observation becomes:

$$y_i = C_0 + C_1 x_{i,1} + C_2 x_{i,2} + \ldots + C_i x_{i,k} + \epsilon_i \tag{2}$$

In this report $x_{i,1}$, $x_{i,2}$, $x_{i,3}$, and $x_{i,4}$ are measurements of the proximate analysis parameters, M, A, VM, and FC, respectively; y_i is the measured calorific values, Q; and ϵ_i is the error associated with the ith lignite sample. It is C_1, C_2, C_3, C_4 that are sought here since we found that the addition of C_0 did not measurably improve the accuracy of the equation and, hence, we have taken $C_0 = 0$.

In matrix algebra the equation for the least squares linear equation is

$$\mathbf{X^T \cdot X \cdot Y = X^T \cdot Z} \tag{3}$$

X, $\mathbf{X^T}$, **Y** and **Z** are matrices with the following definitions and physical interpretations.

$$\mathbf{X} = \begin{vmatrix} M_1^{-1} & A_1 & VM_1 & FC_1 \\ \vdots & \vdots & \vdots & \vdots \\ M_{23}^{-1} & A_{23} & VM_{23} & FC_{23} \end{vmatrix}$$

where M_i is the % moisture for sample i, A_i is the % ash for sample i, VM_i is the % volatile matter for sample i, FC_i is the % fixed carbon for sample i, and

$$M_i + A_i + VM_i + FC_i = 100 \tag{4}$$

Thus, **X** contains the proximate analysis data for all 23 available samples. M^{-1} was used because it gave a better fit than M. $\mathbf{X}^T$ (**X** transpose) is obtained from **X** by simply exchanging rows for columns or vice versa, i.e.,

$$\mathbf{X}^T = \begin{vmatrix} M_1^{-1} \dots M_{23}^{-1} \\ A_1 \dots A_{23} \\ VM_1 \dots VM_{23} \\ FC_1 \dots FC_{23} \end{vmatrix}$$

Y is the solution matrix and contains the coefficients we seek for the equation:

$$Q = C_1 M_1^{-1} + C_2 A + C_3 VM + C_4 FC \tag{5}$$

$$\mathbf{Y} = \begin{vmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \end{vmatrix}$$

where C_1 is the best fit coefficient for M^{-1}, C_2 is the best fit coefficient for A, C_3 is the best fit coefficient for VM, C_4 is the best fit coefficient for FC. Finally **Z** is defined as

$$\mathbf{Z} = \begin{vmatrix} Q_1 \\ \vdots \\ Q_{23} \end{vmatrix}$$

where Q_i is the calorific value of lignite i in BTU/lb. **X**, $\mathbf{X}^T$, **Y**, and **Z** are 23×4, 4×23, 4×1, and 23×1 matrices, respectively. Matrix multiplication of $\mathbf{X}^T$ by **X**, $(\mathbf{X}^T \cdot \mathbf{X})$, results in the 4×4 matrix $\mathbf{X}^*$; similarly, $\mathbf{X}^T \cdot \mathbf{Z}$ yields the 4×1 matrix $\mathbf{Z}^*$. These are defined as

$$\mathbf{X}^* = \begin{vmatrix} a_{1,1} & a_{1,2} & a_{1,3} & a_{1,4} \\ a_{2,1} & a_{2,2} & a_{2,3} & a_{2,4} \\ a_{3,1} & a_{3,2} & a_{3,3} & a_{3,4} \\ a_{4,1} & a_{4,2} & a_{4,3} & a_{4,4} \end{vmatrix} \text{ and } \mathbf{Z}^* = \begin{vmatrix} a_{1,5} \\ a_{2,5} \\ a_{3,5} \\ a_{4,5} \end{vmatrix}$$

Multiplying $\mathbf{X}^* \cdot \mathbf{Y}$ and setting that equal to $\mathbf{Z}^*$ produces a set of four

equations (6a)–(6d) with four unknowns, C_1, C_2, C_3, and C_4.

$$a_{1,1}C_1 + a_{1,2}C_2 + a_{1,3}C_3 + a_{1,4}C_4 = a_{1,5} \tag{6a}$$

$$a_{2,1}C_1 + a_{2,2}C_2 + a_{2,3}C_3 + a_{2,4}C_4 = a_{2,5} \tag{6b}$$

$$a_{3,1}C_1 + a_{3,2}C_2 + a_{3,3}C_3 + a_{3,4}C_4 = a_{3,5} \tag{6c}$$

$$a_{4,1}C_1 + a_{4,2}C_2 + a_{4,3}C_3 + a_{4,4}C_4 = a_{4,5} \tag{6d}$$

Now, using Gauss reduction as the algorithm to solve these equations, (6a)–(6d) become (9a)–(9d) through the application of eqns. (7) and (8) which are easily programmed on a computer:

$$\alpha_{i,j} = \frac{a_{i,j}^{(i-1)'}}{a_{i,i}^{(i-1)'}} \tag{7}$$

$$a_{i,j}^{n'} = a_{i,j}^{(n-1)'} - a_{i,n}^{(n-1)'}\left(\alpha_{n,j}^{(n-1)'}\right) \tag{8}$$

i.e.,

$$\alpha_{1,3} = a_{1,3}/a_{1,1} \qquad a'_{2,3} = a_{2,3} - a_{2,1}\alpha_{1,3}$$

$$\alpha_{3,4} = a''_{3,4}/a''_{3,3} \qquad a'''_{4,4} = a''_{4,4} - a''_{4,3}\alpha_{3,4}$$

$$C_1 + \alpha_{1,2}C_2 + \alpha_{1,3}C_3 + \alpha_{1,4}C_4 = \alpha_{1,5} \tag{9a}$$

$$a'_{2,2}C_2 + a'_{2,3}C_3 + a'_{2,4}C_4 = a'_{2,5} \tag{9b}$$

$$a'_{3,2}C_2 + a'_{3,3}C_3 + a'_{3,4}C_4 = a'_{3,5} \tag{9c}$$

$$a'_{4,2}C_2 + a'_{4,3}C_3 + a'_{4,4}C_4 = a'_{4,5} \tag{9d}$$

Applying (7) and (8) to (9b), (9c), and (9d) yields:

$$C_1 + \alpha_{1,2}C_2 + \alpha_{1,3}C_3 + \alpha_{1,4}C_4 = \alpha_{1,5} \tag{10a}$$

$$C_2 + \alpha_{2,3}C_3 + \alpha_{2,4}C_4 = \alpha_{2,5} \tag{10b}$$

$$a''_{3,3}C_3 + a''_{3,4}C_4 = a''_{3,5} \tag{10c}$$

$$a''_{4,3}C_3 + a''_{4,4}C_4 = a''_{4,5} \tag{10d}$$

and continuing through two more reductions produces:

$$C_1 + \alpha_{1,2}C_2 + \alpha_{1,3}C_3 + \alpha_{1,4}C_4 = \alpha_{1,5} \tag{11a}$$

$$C_2 + \alpha_{2,3}C_3 + \alpha_{2,4}C_4 = \alpha_{2,5} \tag{11b}$$

$$C_3 + \alpha_{3,4}C_4 = \alpha_{3,5} \tag{11c}$$

$$C_4 = \alpha_{4,5} \tag{11d}$$

which allows for the solution of the four unknowns. In particular, working back from (11d) to (11a) allows solution of C_4 through C_1. These values $C_1 = -2.363 \times 10^5$, $C_2 = 107.7$, $C_3 = 297.4$, and $C_4 = 281.1$, were thus obtained. It is not necessary to perform matrix algebra in order to get a least squares best fit. There are computer programs that perform various kinds of regressions which will also give a least squares best fit analysis.

RESULTS

So the equation arrived at to calculate heating values of lignites from proximate analysis data is

$$Q = -2.26 \times 10^5 \, M^{-1} + 108A + 297VM + 281FC \tag{12}$$

where Q is the calorific value in BTU/lb. The best-fit equation (12), determined as described above, yielded an average deviation of only $\pm 1.2\%$ when compared to the experimentally determined calorific values supplied to us by the Pennsylvania State University Coal Research Laboratory. It is interesting to note that the calculated coefficients for VM and FC are nearly equal (297 and 281, respectively) differing by only 5.8%. This was also true for the equations arrived at for higher rank coals by Goutal [2] and by Earnest and Fyans [3]. Because FC = 100 − VM − M − A, it is not really an independent variable. However, since it has historically been included in equations relating Q to proximate analysis, we include it in our analysis. If

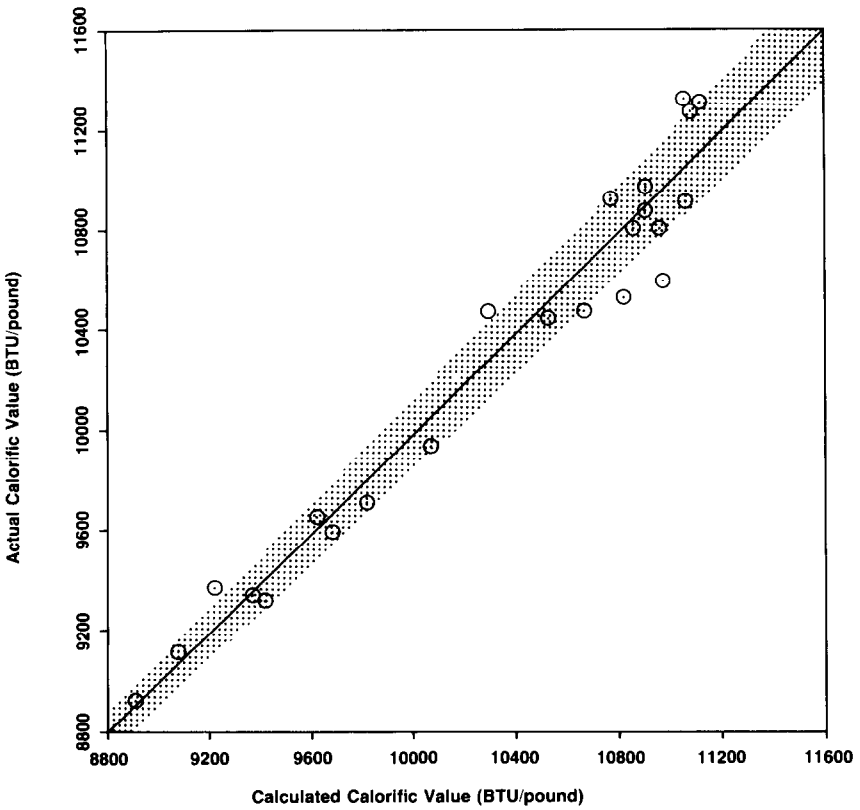

Fig. 1. Plot of actual versus calculated calorific values for 23 lignites. The shaded area represents $\pm 1.2\%$ from perfect agreement. The agreement is reasonably good.

TABLE 1

Description of lignite samples used in this study, including calculated and measured calorific value (Q)

PSOC No.	Seam name	Source	Q measured (BTU/lb.)	Q calculated (BTU/lb.)	ϵ (%)
86	Zap	North Dakota	10812	10847	0.33
88	Zap	North Dakota	10531	10817	2.7
90	Lower Lignite	Montana	10811	10956	1.3
91	Lower Lignite	Montana	10922	11053	1.2
92	Lower Lignite	Montana	10977	10902	0.69
93	Lower Lignite	Montana	10684	10657	0.26
140	Darco Lignite	Texas	11324	11052	2.4
141	Darco Lignite	Texas	11322	11105	1.9
245	Upper Gascoyne	North Dakota	10445	10519	0.71
246	Hagel	North Dakota	10596	10966	3.5
247	Noonan	North Dakota	10871	10988	0.25
413	Darco Lignite	Texas	10483	10280	1.9
417	Unnamed	Texas	9906	9834	0.73
418	Unnamed	Texas	9348	9360	0.13
419	Unnamed	Texas	9369	9209	1.7
625	Darco Lignite	Texas	9652	9619	0.34
789	Unnamed	Texas	9312	9410	1.0
790	Unnamed	Texas	9589	9677	0.92
791	Unnamed	Texas	9939	10065	1.3
793	Unnamed	Texas	8922	8906	0.19
833	Fort Union Bed	Montana	9114	9070	0.49
1036	Unnamed	Texas	10939	10768	1.6
1038	Unnamed	Texas	11283	11087	1.7

it were eliminated the coefficient for VM would be approximately doubled. The fit of the calculated versus the experimental values is exhibited visually on Fig. 1. The shaded area on Fig. 1 is representative of an uncertainty of 1.2%. Agreement between the calculated and experimental values is good. Data are summarized in Table 1. We can offer no rational explanation for the presence of the reciprocal of the moisture content in the equation. It simply gives the best fit.

DISCUSSION

Many recent studies [3–13] have shown that the thermogravimetric method for conducting proximate analysis is a rapid and reliable method for quality control in fossil fuel research. Furthermore, the Goutal [2] equation was recently rediscovered independently by Earnest and Fyans [3] and Rowe [11]. Thus, not only may one obtain the proximate analysis of coal by thermogravimetry, but the calorific value may be determined indirectly from

their data using the Goutal equation for bituminous coals containing 5–35% DAF volatile matter with an average error of $\leqslant 2\%$ compared with oxygen bomb calorimetry. Earnest and Fyans [3] developed a modified form of the Goutal equation to determine the calorific value of anthracitic coals and cokes. We now present an equation which is accurate for a variety of lignites.

Thus, in summary, it is now possible to arrive at an accurate estimate of the calorific value of most coals with a 30-min thermogravimetric measurement of the proximate analysis and the use of either the Goutal equation (for bituminous coals, with DAF volatile matter content of 5–35%), the Earnest–Fyans equation for anthracitic coals and cokes, or the equation developed here for lignites. The average error between our calculated values and the values measured by bomb calorimetry provided by the Pennsylvania State University Coal Research Laboratory is only $\pm 1.2\%$ for the 23 lignite samples as is shown graphically in Fig. 1.

The sample set may not be large enough to be statistically valid for other lignite samples. The 23 samples are not independent, since they include several sets of samples, members of each set being from the same site and often comprising a channel sample of the whole seam plus three arbitrary subsections of the same seam. It may ultimately be necessary to derive more than one equation to accommodate all the lignites.

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NOMENCLATURE

A_i	% ash in lignite i
$a_{i,j}$	a matrix element without physical meaning
C_0	an additive constant
C_1	best fit coefficient for M^{-1}
C_2	best fit coefficient for A
C_3	best fit coefficient for VM
C_4	best fit coefficient for FC
FC_i	% fixed carbon in lignite i
M_i	% moisture in lignite i
Q	calorific value (BTU/lb)
VM_i	% volatile matter in lignite i

Matrices

$\mathbf{X}$ matrix containing proximate analysis data
$\mathbf{X}^T$ $\mathbf{X}$ transpose
$\mathbf{X}^*$ a matrix used in determining C_1, C_2, C_3, and C_4
$\mathbf{Y}$ solution matrix
$\mathbf{Z}$ matrix containing calorific value data
$\mathbf{Z}^*$ a matrix used in determining C_1, C_2, C_3, and C_4

Greek letters

$\alpha_{i,j}$ matrix element in Gauss reduction
ϵ error in calculated calorific value

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