

FORMULAS FOR CALCULATING THE HEATING VALUE OF COAL AND COAL CHAR: DEVELOPMENT, TESTS AND USES

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The heating (calorific) value of coal and char is of great importance in the conversion of coal to other useful forms of fuel, as well as in its direct use. The significance of the correlation of heating value with composition in ordinary fuel usage is shown by the development, as early as 1940, of some 9 different formulas for calculating heating value from the ultimate analysis and 11 formulas for calculating it from the proximate analysis (1). Three additional ultimate analysis formulas have been proposed within the last three years (2,3,4). The correlation is perhaps of even greater importance for the rationalization and modeling of conversion processes now being developed.

Our own work on this problem was carried out for a project on preparation of a "Coal Conversion Systems Technical Data Book," supported by the U.S. Department of Energy and its predecessors.

A data base (including experimental heating values, ultimate analyses and some other parameters) was established, consisting of 121 samples from the Coal Research Section of Pennsylvania State University (5), and 681 samples analyzed by the Bureau of Mines and reported in various state and Federal government publications (6,7,8,9). The Penn State samples, representing large deposits of coal, had been selected for tabulation in the Data Book (10). The data base covers a wide range of coal fields of the United States.

Four formulas were selected for test. They are as follows:

Dulong (1)

$$Q = 145.44 C + 620.28 H + 40.5 S - 77.54 (O) \quad 1)$$

Boie (11)

$$Q = 151.2 C + 499.77 H + 45.0 S - 47.7 (O) + 27.0 N \quad 2)$$

Grummel and Davis (1,12)

$$Q = \left[\frac{654.3 H}{(100-A)} + 424.62 \right] [C/3 + H - (O)/8 + S/8] \quad 3)$$

Mott and Spooner (1,13)

$$Q = 144.54 C + 610.2 H + 40.5 S - 62.46 (O) \quad (O) \leq 15\% \quad 4a)$$

$$Q = 144.54 C + 610.2 H + 40.5 S - \left[65.88 - \frac{30.96(O)}{(100-A)} \right] (O) \quad (O) > 15\% \quad 4b)$$

In the above, Q is the gross heating value in Btu/lb on the dry basis and C, H, S, (O), N, and A are the respective contents of carbon, hydrogen, sulfur, oxygen, nitrogen, and ash in weight percent, also on the dry basis.

For a fair test of the formulas on samples representing commercial coal we eliminated samples with more than 30% ash, leaving a total of 775 samples in the data bank. Results of applying the several formulas separately to the various ranks of coal and also to the combined (all ranks) data are presented in Table 1. The bias (average algebraic difference between observed and calculated values) and the standard deviation after correction for the bias are the most significant criteria. For most of the formulas there are large differences in bias among different ranks of coal, so we have calculated standard deviations for each rank after correcting for the bias shown for that rank. The standard deviation is also given with application of a bias correction averaged over all ranks. Note that the often-used Dulong formula has a substantial bias for all ranks, but of opposite sign for low-rank coals compared with bituminous and anthracite coals. Thus the overall bias is low, but no advantage is gained by its application. Also note that although results from the Boie equation have the highest bias of any, after application of an overall bias correction the results are among the best.

In addition to calculation with the formulas per se, we also calculated heating values by use of Given and Yarzab's modified Parr equation for mineral matter content, and their corrections to obtain carbon, hydrogen, sulfur and oxygen on a mineral-matter-free basis (14). This calculation requires values for pyritic sulfur that were not available for some of the samples. Results obtained with the modified Mott-Spooner equations on 646 samples having pyritic sulfur contents are also shown in Table 1; results from other formulas were improved, but the Mott-Spooner equation gave the best results. Details of this calculation and full results are reported elsewhere (15).

The data bank was also subjected to a least squares regression analysis. Carbon, hydrogen, sulfur, ash, and oxygen terms were significant; nitrogen and cross and square terms were not. To avoid the implied necessity of determining nitrogen, we adopted an oxygen-plus-nitrogen term. The resulting equation, which we refer to here as the Data Book Equation, was as follows:

$$Q = 146.58 C + 568.78 H + 29.4 S - 6.58 A - 51.53 (O + N) \quad 5a)$$

When 100- C-H-S-A is substituted for O+N, an equivalent form is obtained:

$$Q = 198.11 C + 620.31 H + 80.93 S + 44.95 A - 5153 \quad 5b)$$

Results from this new formula are also shown in Table 1. The bias for different ranks of coal ranges only from -45 Btu/lb on lignite to 13 Btu/lb on subbituminous coal and does not show a trend with rank. The standard deviation is significantly less than those of the other unmodified formulas, even after improving these by a bias correction. The new formula has about the same accuracy as the Mott-Spooner with modified Parr corrections, but the latter is more complicated and requires pyritic sulfur determination.

The effect of ash content on the accuracy and precision of the formula was investigated, with the results shown in Table 2. For this test, the formula was also applied to the 27 high-ash samples that had been removed from the data bank.

Table 1. TEST OF FORMULAS FOR CALCULATION OF HEATING VALUE

				Standard Deviation		
	No. of Samples	Average Absolute Deviation	Bias*	Before Bias Correction	After Rank Bias Correction	After Over- all Bias** Correction
				Btu/lb		
<u>Dulong</u>						
Anthracite	40	137	-123	157	97	146
Bituminous	406	181	-138	221	173	212
Subbituminous	130	174	127	213	170	222
Lignite	149	218	174	255	185	266
All Ranks	775	184	-15	223	—	222
<u>Boie</u>						
Anthracite	40	400	-400	417	100	177
Bituminous	406	253	-248	279	129	129
Subbituminous	180	217	-207	249	138	146
Lignite	149	301	-298	330	138	145
All Ranks	775	262	-256	291	—	139
<u>Grummel and Davis</u>						
Anthracite	40	107	79	134	106	165
Bituminous	406	164	-128	208	164	184
Subbituminous	180	130	46	168	161	185
Lignite	149	127	39	171	167	187
All Ranks	775	146	-44	189	—	184
<u>Mott and Spooner</u>						
Anthracite	40	84	-56	107	91	100
Bituminous	406	160	-134	197	144	149
Subbituminous	180	113	-31	152	149	162
Lignite	149	124	-85	170	147	147
All Ranks	775	138	-96	178	—	150
<u>Mott & Spooner, Modified Parr Basis</u>						
All Ranks	646	106	42	—	—	132
<u>New Formula</u>						
Anthracite	40	73	-14	93	92	93
Bituminous	406	90	10	124	123	124
Subbituminous	180	103	13	140	139	140
Lignite	149	96	-45	137	129	137
All Ranks	775	93	0	129	129	129

* Average observed value — average calculated value

** Bias obtained over all ranks

Table 2. EFFECT OF ASH CONTENT ON THE CALCULATION OF HEATING VALUE

Ash Content, wt %	Number of Samples	Avg. Absolute Difference	Bias*	Standard Deviation
0-10	394	82	6	113
10-20	320	104	-15	144
20-30	61	112	26	141
>30	27	155	20	211

* Average of observed minus average of calculated values

The absence of significant bias, here and among different ranks of coal, indicates that no improvement by change in the formula appears possible as long as it is based on ultimate analysis only. The increase of the standard deviation with ash content can be attributed to the effects of differing ratios of mineral matter to ash, and differing contributions of the mineral matter to determined carbon and hydrogen contents. A computer analysis of the data in which it was assumed that the variance is linear with ash content indicated that the variance increases by $4/2$ (Btu/lb)² per percent of ash, and that the standard deviation on ash-free samples would be 106 Btu/lb.

It is of interest to determine whether the remaining variance can actually be attributed to the laboratory determinations. The latter can be estimated according to —

$$\text{Var (exp)} = \text{Var Q} + 198.11^2 \text{ Var C} + 620.31^2 \text{ Var H} \\ + 80.93^2 \text{ Var S} + 44.95^2 \text{ Var A} \quad 6)$$

where Var Q, Var C, etc., are variances of the respective determinations. Some precision data have become available from the HYGAS® program at ICT, which can be used for a test.

Sources of variance of the experimental determinations need to be considered for the purpose at hand. The heating value and the analytical determinations (carbon, hydrogen, sulfur, and ash) are all run on a sample of coal (or char) that has been ground finer than 60-mesh sieve size. Thus, the variance from sampling of the coarse sample submitted to the laboratory is not of concern. If the moisture content does not change during all of the sample withdrawals for the various determinations, no variance is contributed by the moisture determination; however, if several days elapse between heating value and carbon-hydrogen determinations, a contribution from this source is likely, either from the change in moisture or from the variance of its redetermination. Variance can also be contributed by day-to-day variations in equipment and operator; thus redetermination on the same day would not serve the purpose. Instead, our procedure consisted of resubmitting from time to time a number of ground samples of coal (in the same 4-oz bottles as originally sampled from) for redetermination of moisture, heating value, carbon, hydrogen, sulfur, and ash. Each reported value for carbon, hydrogen, ash, and heating value is the average of two determinations run at the same time; for sulfur only one determination is made. Completion of the duplicate analysis ranged from 9 to 46 days after completion of the routine analysis. Slight average changes in values from the original analysis to the duplicate, such as an average decrease in heating value of 13 Btu/lb, occurred; the standard deviations were calculated both with and without correction for this bias.

The duplicate differences from this program were examined for outliers. Three sulfur, one ash and one heating value, all with differences between duplicates greater than $3.8 \sqrt{2} \sigma$, were discarded. In addition, a heating value with a duplicate difference of $2.8 \sqrt{2} \sigma$, and also having a difference between observed and calculated values of 3.5σ was also discarded. The analysis of the remaining data is presented in Table 3.

The variance contributed to the difference between observed and calculated heating values by the variance of the experimental determinations can now be calculated according to Equation 6. The standard deviations after bias corrections (Table 3) yields the value 64 Btu/lb as the expected σ . This represents 77% of the variance found for a large set of routine HYGAS data on raw bituminous coal discussed later in this paper. The remainder of the variance can be attributed to the effect of outlying laboratory determinations, and the effect of mineral matter.

Table 3. SUMMARY OF HYGAS REPEATABILITY DATA

	No. of Duplicates	Average Value	Bias*	Standard Deviation**	
				Before Bias Correction	After Bias Correction
Heating Value	56	11680	13	Btu/lb	
				29	27
				wt %	
Carbon	41	64.07	0.037	0.25	0.24
Hydrogen	41	4.52	0.028	0.051	0.051
Sulfur	55	4.39	-0.011	0.084	0.086
Ash	40	16.77	0.037	0.14	0.14

* Original minus duplicate

** Of reported values, each the average of two determinations run at the same time, except single determinations for sulfur.

TEST AND USES

Data for testing of the new formula were solicited from outside laboratories. Results from two laboratories presented in Table 4 show good precision, but the large bias values suggest the presence of systematic error or difference from the original data.

Results from a third laboratory illustrate an important use of the formula. The experimental data covered a period of several years and were furnished in the sequence in which they were obtained by the laboratory. We eliminated a few samples having over 35% ash or less than 3% oxygen, because the latter are likely to be chars. On the remaining data, the standard deviations obtained from consecutive sets of 50 samples are shown in Figure 1. On the first 650 samples the bias was 32 Btu/lb and the standard deviation was 136 Btu/lb, in good agreement with results on the original data bank. On subsequent samples the results indicate a substantial deterioration in laboratory precision. Thus, a control chart of this kind can serve as a monitor of laboratory performance. Also, the difference between observed and calculated heating values on an individual sample can be used by the laboratory supervisor as a criterion of acceptability of the heating value and carbon-hydrogen determinations. The difference is less sensitive to the sulfur and ash values.

Table 4. TESTS OF NEW HEATING VALUE FORMULA AT OTHER LABORATORIES

Laboratory	Kind of Coal	No. of Samples	Average Absolute Difference	Bias*	Standard Deviation	
					Before Bias Correction	After Bias Correction
					Btu/lb	
A	Bituminous	42	115	-96	157	123
B	Illinois Basin	78	112	-91	139	107
B	Subbituminous	40	81	-50	102	90

*: Average observed value minus average calculated value

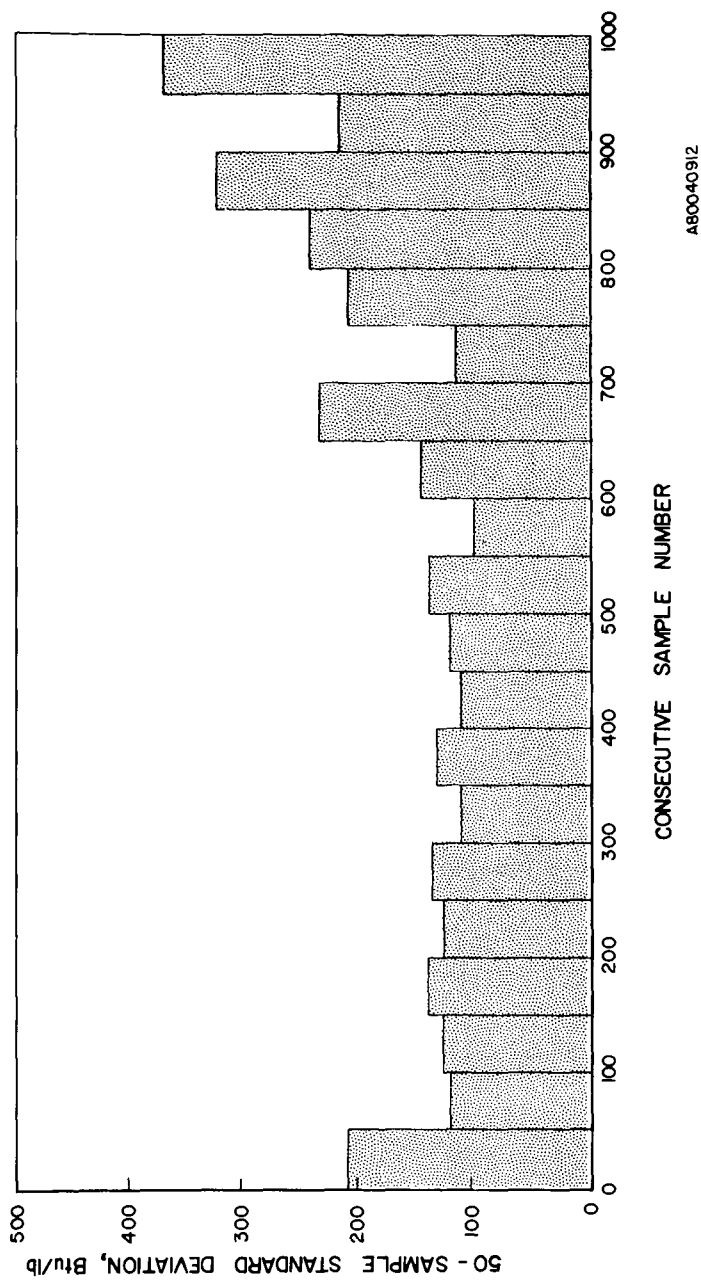


Figure 1. VARIABILITY OF THE DIFFERENCE BETWEEN OBSERVED AND CALCULATED HEATING VALUE IN ONE LABORATORY

Another important use of a heating value formula is in computer modeling of coal conversion processes. Data on heating value and composition of samples of coal and char obtained at IGT under the HYGAS pilot plant program were analyzed for this purpose. In the HYGAS process, non-agglomerating coals are dried but are not otherwise pretreated. Bituminous coals are pretreated at temperatures of 750°F to 800°F to destroy their agglomerating properties. The resulting product is referred to here as "pretreated coal" rather than "char". Samples referred to as "chars" are from later intermediate stages or are spent (residue) char. Ash in the spent char from the runs on bituminous coal averaged 36%, but ranged up to about 85%. To augment the data from runs on subbituminous and lignite coals, we have added some samples taken from streams that contain feed coal in addition to char, such as the dust collected by a cyclone in the reactor product gas stream. Results are presented in Table 5, together with those obtained on the original data bank.

The most important criterion for use of a heating value formula in a computer model of a coal conversion process is the bias or average difference between observed and calculated values, because it shows how closely the formula represents the properties of the coal. On the 294 samples of raw (untreated) bituminous coals, the calculated values are, on the average, 18 Btu/lb less than the observed values. This differs by only 8 Btu/lb from the value found on the 406 samples of bituminous coal in the original data bank. There is only about a 20 percent chance that the difference is significant; if so, it can be attributed to a slightly lower ash content obtained at IGT, because at IGT the amount of sulfur trioxide in ash is routinely determined and deducted from the reported ash. Ash as customarily determined is likely to contain small amounts of sulfur trioxide.

The standard deviation shown for these coal samples is substantially less than was found on the bituminous coals of the original data bank. The difference may be a result of the limited range of source of the HYGAS samples: all were from the Illinois No. 6 seam and 95% were from a single mine; the ash content averaged 10.7%. (The samples from the repeatability set of data had higher ash, averaging about 17%).

On pretreated bituminous coal the calculated values are, on the average, 157 Btu/lb lower than the observed values. The Data Book formula is thus unsatisfactory for use in a computer model applied to this material; for such use a bias correction can be applied or a formula can be obtained by regression analysis of the pretreated coal data. The difference in bias between the parent and pretreated coal, 139 Btu/lb, can be attributed to a difference in structure (bonding); the formula has already taken into account differences in elemental composition. Such differences in structure include effects of incorporation of oxygen in a different form from that ordinarily present. In other processes the difference in bias may be greater or less, depending on processing conditions such as temperature and presence or absence of oxygen; in the HYGAS process the difference is reduced to about 40 Btu/lb at the stage where the temperature reaches about 1200°F.

On the set of samples of char from bituminous coals the calculated values are, on the average, only 28 Btu/lb less than the observed values; the difference is of about the same order for chars from subbituminous coal and lignite. A more accurate formula could be obtained for the chars from the bituminous coal, but the Data Book formula should be adequate for most practical purposes; the accuracy should be judged according to unit weight of coal feed rather than unit weight of char.

CONCLUSIONS

A new five-term formula for calculating the heating value of coal from its carbon, hydrogen, sulfur and ash content was obtained by regression analysis of data on 775 samples of U. S. coals of all ranks. The standard deviation of the calculated value from the observed value was 129 Btu/lb, compared to apparent standard deviations ranging from 178 to 229 Btu/lb obtained from the Dulong, Boie, Grummel and Davis, and Mott and Spooner formulas. An analysis of the variance of the difference between

Table 5. TEST ON HYGAS ROUTINE SAMPLES OF THE DATA BOOK FORMULA
FOR CALCULATION OF HEATING VALUE

HYGAS Data Bank	No. of Samples	Bias ^d	Standard Deviation	
			Before Bias Correction	After Bias Correction
			Btu/lb	
Bituminous Coal ^a				
Raw Coal	294	18	73	71
Pretreated Coal	572	157	174	76
Chars				
First Stage Hydrogasification	105	58	98	79
Second Stage Hydrogasification	106	2	106	106
Spent Char	570	28	97	92
All Char	781	28	98	94
Subbituminous Coal ^b				
Coal	49	-47	69	51
Chars	80	15	59	57
Mixtures of Coal and Char	66	15	55	53
Lignite ^c				
Chars	80	34	78	77
Mixtures of Coal and Char	44	12	88	77
Original Data Bank				
Bituminous Coal	406	10	124	124
Subbituminous Coal	180	13	140	140
Lignite	149	-45	137	137
All Samples, Including Anthracite	775	0	129	129

^a From Illinois No. 6 seam. About 1/8 of the samples were from runs on hvBb coal from Saline County, and the remainder from runs on hvCb coal from Christian County.

^b From the Rosebud Seam, Rosebud County, Montana.

^c From the Savage Mine, Richland County, Montana.

^d Average observed value minus average calculated value.

observed and calculated values obtained with the new formula on IGT coal data indicated that at least 77% is contributed by the variance of the experimental determinations; the remainder can be attributed to the effect of mineral matter and outlying experimental determinations.

Application of the formula to coal oxidatively pretreated at 750°F to 800°F to destroy agglomerating properties yields a bias indicating that its heat of formation is higher than expected from elemental and ash composition by about 140 Btu/lb; this is attributed to differences in structure (bonding) of the pretreated coal in comparison to unpretreated coal. The formula gives satisfactory results on higher temperature HYGAS chars, and, with application of a bias correction, on pretreated coal

Thus, the formula is advantageous for use in the computer modelling of coal conversion processes and for monitoring test data on coal and char.

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LITERATURE CITED

1. Selvig, W. A. and Gibson, F. H., "Calorific Value of Coal," in Lowry, H. H., ed., Chemistry of Coal Utilization 1, 139. New York: John Wiley, 1945.
2. Subramaniam, T. K., "How to Calculate Btu Values of Coal," Coal Age, 82, 153-58 (1977) December
3. Lloyd, W. G. and Francis, H. E., Personal Communication, 1979.
4. Lloyd, W. G. and Davenport, D. A., "Applying Thermodynamics to Fossil Fuels," J. Chem. Ed. 57, 56-60 (1980) January.
5. Spackman, W. et al., "Evaluation and Development of Special Purpose Coals, Final Report" ERDA No. FE-0930-2, NTIS, Springfield, Va. 1976.
6. Swanson, V. E. et al., "Collection, Chemical Analysis, and Evaluation of Coal Samples in 1975," U.S. Department of the Interior, Geological Survey, Open-File Report 76-468, 1976.
7. Gilmour, E. H. and Dahl, G. G., Jr., "Montana Coal Analyses," Bur. Mines Geol. Spec. Publ. 43. Butte, Mont. 1976.
8. Glass, G. B., "Analyses and Measured Sections of 54 Wyoming Coal Samples (Collected in 1974)," Geological Survey of Wyoming Rep. Invest. No. 11. Laramie, Wyo. 1975.
9. Sondreal, E. A., Kube, W. R. and Elder, J. L., "Analysis of the Northern Great Plains Province Lignites and Their Ash," U.S. Bur. Mines Rep. Invest. No. 7158. Washington, 1968.
10. Institute of Gas Technology, "Coal Conversion Systems Technical Data Book," U.S. Department of Energy No. HCP/T2286-01, Supt. of Documents, Washington, D.C. 1978.
11. Boie, W., "Fuel Technology Calculations," Energietechnik 3, 309-16 (1953).
12. Grummel, E. S., and Davis, I. A., "A New Method of Calculating the Calorific Value of a Fuel From Its Ultimate Analysis," Fuel 12, 199-203 (1933).

13. Mott, R. A., and Spooner, C. E., "The Calorific Value of Carbon in Coal," Fuel 19, 226-31, 242-51 (1940).
14. Given, P. and Yarzab, R. F., "Problems and Solutions in the Use of Coal Analyses. Technical Report 1." ERDA No. FE-0390-1. NTIS, Springfield, Va. 1975.
15. Institute of Gas Technology, "Preparation of a Coal Conversion Systems Technical Data Book," ERDA No. FE-2286-32, NTIS, Springfield, Va. 1978.