E., Ed.; The Chemical Society, London, 1958.
De Santis, R.; Breedveld, G. J. F.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1974**, *13*, 347.
Chappelow, C. C.; Prausnitz, J. M. *AIChE J.* **1974**, *20*, 1097.
Coan, C. R.; King, A. D. *J. Am. Chem. Soc.* **1971**, *93*, 1857.
Cukor, P. M.; Prausnitz, J. M. *J. Phys. Chem.* **1972**, *76*, 598.
Edwards, D.; Van de Rostyne, C. G.; Winnick, J.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 138.
Gonzales, C. M.S. Thesis, University of California, Berkeley, CA, 1980.
Hankinson, R. W.; Thomson, G. H. *AIChE J.* **1979**, *25*, 4.
Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. "Molecular Theory of Gases and Liquid", 1st ed.; Wiley: New York, 1954; p 158.
Kaul, B. K.; Prausnitz, J. M. *AIChE J.* **1978**, *24*, 223.
King, C. J. "Separation Processes", 1st ed.; McGraw-Hill: New York, 1971; p 513.
Lyckman, E. W.; Eckert, C. A.; Prausnitz, J. M. *Chem. Eng. Sci.* **1965**, *20*, 685.
Macknick, A. B.; Prausnitz, J. M. *AIChE J.* **1978**, *24*, 4.
Macknick, A. B. Ph.D. Dissertation, University of California, Berkeley, CA, 1979.
Moelwyn-Hughes, E. A. "Physical Chemistry", 2nd ed.; Pergamon Press: New York, 1965; p 491.
Monge, A.; Prausnitz, J. M. In "Chemical Engineering at Supercritical-Fluid Conditions"; Paulaitis, M. E.; Penninger, J. M. L.; Grey, R. D., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1983. See also *Ind. Eng. Chem. Fundam.* **1983**, *22*, 505.
Monge, A. Ph.D. Dissertation, University of California, Berkeley, CA, 1982.
Nokay, R. *Chem. Eng.* **1959**, *66*, 4.
Nothnagel, K. H.; Abrams, D. S.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1973**, *12*, 25.
Sherwood, A. E.; Prausnitz, J. M. *J. Chem. Phys.* **1964**, *41*, 429.
Smith, G.; Winnick, J.; Abrams, D. S.; Prausnitz, J. M. *Can. J. Chem. Eng.* **1976**, *54*, 337.
Tremper, K. K.; Prausnitz, J. M. *J. Chem. Eng. Data* **1976**, *21*, 295.

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Heat of Combustion of Green River Oil Shale

Michael J. Muehlbauer and Alan K. Burnham*

Lawrence Livermore National Laboratory, Livermore, California 94550

We derive simple equations for estimating the heat of combustion of raw shale by thermochemical estimates and by linear regression of experimental data. We find that the heat can be estimated well by an exothermic term that accounts for the combustion of organic matter and a constant that accounts for pyrite combustion, carbonate decomposition, and glass formation. The net contribution of reactions included in the constant is endothermic for the standard state products of bomb calorimetry. As a sample application, we perform an energy balance on a modified Fischer assay of average Green River shale by using one of our formulas for raw shale along with previously derived formulas for pyrolysis products.

Introduction

In making a heat balance for adiabatic oil shale retorting experiments, the sensible and chemical heat content of the raw shale and other reactants is compared to the sum of the heat contents of the products including the oil, retorted shale, and gas. A value for the heat of combustion of raw shale, $(-\Delta H_c)_{rs}$, is frequently needed for this balance, especially for combustion retorting. If an experimental value for $(-\Delta H_c)_{rs}$ is not available, a value must be estimated using thermochemical considerations.

An expression whereby the heat of combustion of raw shale can be estimated quickly from shale composition would be useful. Burnham et al. (1982) have shown in previous work that the heat of combustion (kJ/kg) of retorted (spent) shale could be related to the organic carbon, total sulfur, and mineral CO_2 content by a simple linear equation. Coefficients for the equation were developed through thermochemical reasoning and by multiple linear regression. We expected that a similar expression could be developed for the heat of combustion of raw shale.

In this report, we first derive an expression for the heat of combustion of raw shale based solely on thermochemical theory. Next, using available experimental data, we develop an expression for $(-\Delta H_c)_{rs}$ by a multiple linear regression. The theoretical expression is compared to the regression equation to verify its applicability. Finally, to illustrate the use of the $(-\Delta H_c)_{rs}$ expression, we perform a heat balance to show the redistribution of combustion energy caused by a modified Fischer assay.

Thermochemical Expression for $(-\Delta H_c)_{rs}$

The expression for the heat of combustion of raw shale based on thermochemical theory is

$$(-\Delta H_c)_{rs} = 496\ (\text{wt \% org C}) + 107\ (\text{wt \% S}) - 18\ (\text{wt\% acid } CO_2) - 75 \quad (1)$$

The expression gives heat of combustion in units of kJ/kg.

The first term on the right-hand side of the expression gives the contribution to $(-\Delta H_c)_{rs}$ by the combustion of the organic kerogen. The coefficient was calculated by estimating the heat of combustion of kerogen by the Boie formula (Ringen et al., 1979). The composition of the kerogen was taken to be as reported by Smith (1961): 80.5% C, 10.3% H, 2.39% N, 1.04% S, and 5.75% O.

The second term accounts for the heat of combustion of pyrite (FeS_2) found in the raw shale. Typically 80% of the total sulfur in raw shale is in the form of pyrite, which burns with a heat of combustion of −830 kJ/mol of FeS_2. Combustion products were taken to be Fe_2O_3 and SO_2, which are the standard-state products for a bomb calorimeter.

The third term accounts for the heat of decomposition of carbonates in the shale. The carbonates typically consist of about 2 to 3 parts of dolomite ($CaMg(CO_3)_2$ and one part calcite ($CaCO_3$). Their decompositions are endothermic, hence the negative sign of the wt % acid CO_2 coefficient.

The final term in the expression accounts for the heat of glass formation. Approximately 67% of the initial weight of the raw shale is left as ash after combustion.

Table I. Data Used in Regression Analysis

$(-\Delta H_c)_{rs}$, kJ/kg	wt % org C	wt % acid CO_2	wt % S	sample I.D.
5041	10.77	17.72[e]	0.67	L-2 top[a]
5039	10.63	17.67[e]	0.68	L-2 bottom[a]
4103	8.99	18.86[e]	1.69	L-4 top[a]
7541	16.03	16.50[e]	1.02	L-4 bottom[a]
4148	8.78	19.46	1.7	L-3 top[b]
4077	8.69	18.94	1.7	L-3 top[b]
4379	9.12	19.3	1.7	L-3 top[b]
7924	17.34[f]	15.77[f]	1.1	L-3 bottom[a]
5069	10.81	17.32[e]	0.67	S-11[c]
5088	11.12	16.97[e]	0.69	S-12[c]
5075	10.81	17.32[e]	0.67	S-13[c]
4927	11.35	15.42[e]	0.62	S-15[c]
5156	11.47	16.30[e]	0.65	S-16[c]
4622	10.19	17.43[e]	0.69	S-17[c]
5510[f]	11.83[f]	16.60[f]	0.70	S-19[c]
2165	5.38	14.84[e]	0.99	S-20[c]
5041	10.76	17.72[e]	0.66	S-21[c]
4794	10.67	16.86[e]	0.61	S-24[c]
3815	7.65	18.21	0.40	C[d]
3722	8.46	25.72	0.25	J[d]
4024	8.66	20.08	0.29	A[d]
4513	9.53	18.36	0.53	D[d]
4629	10.03	20.26	0.67	H[d]
6466	13.61	15.87	0.75	B[d]
7350	15.77	20.71	0.72	I[d]
7816	16.64	18.29	0.86	G[d]
10420	21.11	15.28	1.31	EF[d]

[a] See Campbell (1981), p 65. [b] See Tripp (1979). [c] See Campbell (1981), p 64. [d] See Stanfield et al. (1951), p 25. [e] Sum of H_2O-evolved and acid-evolved CO_2 wt %. [f] Value listed in Campbell (1981) is incorrect. Correct values were obtained from Tripp (1979).

About 80% of this forms a glass with an endothermic heat of reaction of roughly 140 kJ/kg.

If information is available only on the wt % organic C in the raw shale, the heat of combustion in kJ/kg can be estimated from

$$(-\Delta H_c)_{rs} = 496 \text{ (wt \% org C)} - 313 \qquad (2)$$

This expression was developed by inserting typical values of wt % S = 0.8 and wt % acid CO_2 = 18 into eq 1, although the pyrite, dolomite, and calcite contributions are variable.

To test the accuracy of these equations, we have compiled in Table I previously reported (Campbell, 1981; Stanfield et al., 1951) heats of combustion and compositions of Colorado oil shale. The standard errors of eq 1 and 2 are 177 and 168 kJ/kg, respectively (d.f. = 27). The slightly lower standard error of the simpler eq 2 implies that the effects of variations in S and acid CO_2 are not significant for $(-\Delta H_c)_{rs}$. Although sufficiently accurate for most applications, these standard errors are about five times greater than our experimental precision, implying that other variable contributions may be important.

Regression Expression for $(-\Delta H_c)_{rs}$

An expression for $(\Delta H_c)_{rs}$ was also developed by multiple linear regression using the data in Table I. Our initial attempt was to fit to the form of eq 1. We obtained an equation for which the residual sum of squares was 20% smaller than that of the thermochemical expression. However, all but the carbon coefficient were thermochemically unreasonable and had very large standard errors. Because of the success of eq 2, we then fitted the data to a carbon coefficient plus intercept and obtained

$$(-\Delta H_c)_{rs} = 490 \text{ (wt \% org C)} - 279 \qquad (3)$$

The standard error for this expression is 169 kJ/kg (d.f. = 25), with r^2 = 0.990. The standard errors for the org C coefficient and intercept were 9.7 and 114.5, respectively. (See Figure 1.)

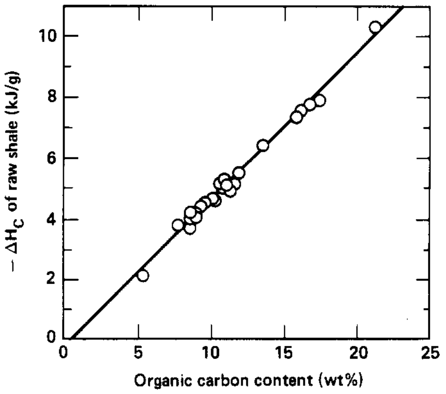

Figure 1. Comparison of experimental data for $(-\Delta H_c)_{rs}$ with that calculated from eq 3.

Table II. Data Used for Comparison of Heat of Combustion Formulas

$(-\Delta H_c)_{rs}$, kJ/kg	wt % org C[b]	wt % acid CO_2	wt % S	sample I.D.[a]
2373	5.09	16.7	0.62	9
5433	12.40	20.0	0.56	8
7164	16.72	18.9	0.73	7
12820	26.12	10.9	1.96	2
13980	28.24	9.9	1.99	1
16280	34.19	10.0	1.86	10

[a] See Stanfield et al. (1951), p 23. [b] Calculated from Cook's formula (Cook, 1974): gal/ton = 2.216 (wt % org C) − 0.7714.

Additional data, which are shown in Table II, were used to compare the theoretical expressions to the regression expression. These data, obtained by Stanfield, orginally did not report the wt % organic C. The modified Fischer-assay yield in gal/ton was reported, however, from which we calculated the composition of organic carbon by Cook's formula (Cook, 1974). Hence the comparison that follows was made with the caution that the organic content was estimated and may not be as accurate as those that were measured.

We calculated values for $(-\Delta H_c)_{rs}$ using the two thermochemical expressions, eq 1 and 2, and the regression expression, eq 3. These values are tabulated, along with the experimental values for $(-\Delta H_c)_{rs}$ in Table III. The standard errors for the three expressions are so nearly equal that the choice of which to use is a matter of preference. Equation 3 is probably most trustworthly because it was developed directly from experimental data. However, eq 1 might be more reliable for Green River oil shales whose compositions are outside the range of these samples.

Heat Balance on a Modified Fischer Assay

To illustrate an application for the heat-of-combustion expression for raw shale, we performed a heat balance on a modified Fischer assay. The basis for the heat balance was an *average* sample of 24.6 gal/ton Green River oil shale weighing 1.0 kg. Information on the compositions of the raw shale and assay products was obtained from a report by Singleton et al. (1982).

The formulas used in calculating the heats of combustion in the pyrolysis heat balance are summarized in Table IV. Formulas are listed for the two conditions of combustion wherein water is present as either liquid or steam in the combustion products. If water appears in the combustion products as steam rather than liquid, the total heat content will be less because the heat of condensation has not been realized. The formula listed for raw shale is the

Table III. Comparison of Additional Experimental Values for Heat of Combustion of Raw Shale (kJ/kg) with Those Calculated by the Three Expressions Developed in This Work

		eq 3 regression		eq 1 theoret		eq 2 theoret	
	exptl obsd	calcd	obsd − calcd	calcd	obsd − calcd	calcd	obsd − calcd
	2 373	2 215	158	2 215	158	2 212	161
	5 433	5 797	−364	5 775	−342	5 837	−404
	7 164	7 914	−750	7 956	−792	7 970	−806
	12 820	12 520	300	12 890	−70	12 630	190
	13 980	13 560	420	13 970	10	13 670	310
	16 280	16 470	−190	16 900	−620	16 650	−370
mean	9 675	9 746		9 952		9 828	
av signed error			−71		−276		−153
std error			413		439		430

Table IV. Formulas Used in Pyrolysis Heat Balance

	$H_2O(l)$ as a Combustion Product
raw shale, kJ/kg	496 (% org C) − 18 (% CO_2) + 107 (% S) − 75
spent shale, kJ/kg	395 (% org C) − 18 (% CO_2) + 170 (% S) − 113
shale oil, kJ/kg	351.5 (% C) + 1162 (% H) + 63 (% N) + 105 (% S) − 111 (% O)
gas	$\Sigma(-\Delta H_{\text{combust.}})$ (mole fraction)
	$H_2O(g)$ as a Combustion Product
raw shale, kJ/kg	474 (% org C) − 18 (% CO_2) + 107 (% S) − 75
spent shale, kJ/kg	389 (% org C) − 18 (% CO_2) + 170 (% S) − 113
shale oil, kJ/kg	351.5 (% C) + 991 (% H) + 63 (% N) + 105 (% S) − 111 (% O)
gas	$\Sigma(-\Delta H_{\text{combust.}})$ (mole fraction)

Table V. Heat Balance for a Modified Fischer Assay of 1 kg of 24.6 gal/ton Green River Oil Shale. Values in Parentheses Are for a Steam Product

	amount	kJ, total material	kJ, organics only
raw shale	1.0 kg	5209 (4964)	5525 (5280)
products:			
retorted shale	0.87 kg	635 (624)	978 (965)
shale oil	0.095 kg	4072 (3886)	4072 (3886)
gas	0.55 mol	422 (382)	422 (382)
total		5129 (4892)	5472 (5233)
difference		80 (72)	53 (47)

three-variable theoretical expression developed in this report. The reported shale formula is that developed by Burnham et al. (1982) from thermochemical estimates. Alternate expressions for the heats of combustion of raw shale and spent shale may be found, respectively, in this report, and in the report by Burnham et al. (1982).

The heat expression used for shale oil is the Boie formula, which can be used for estimating heats of combustion for any low-ash fossel fuel. The heat of combustion of the shale oil may be estimated (if better information is unavailable) using an average composition [84.11% C, 11.44% H, 1.85% N, 0.87% S, and 1.8% O (by difference)], for which $-\Delta H_c = 42870$ kJ/kg. Good approximations for the heat of combustion of the gas, using average compositional data determined by Singleton et al. (1982) (CO, CO_2, H_2, and hydrocarbons up to C_4), are 767 kJ/mol, $H_2O(l)$ basis; and 695 kJ/mol., $H_2O(g)$ basis. Hydrocarbons of C_5 and greater were counted as oil. H_2S in the gas has been ignored.

The results of the heat balance are tabulated in Table V. The heat distribution for the total shale material is listed, as well as the heat distribution for the organic material alone. The heat content of the total shale is less than that of the organics alone because of the endothermic carbonate reactions which occur in the shale inorganics. The lower heating value (steam product) is given in parentheses. The total heat content of the products is very close to that of the raw shale, indicating that the heats of kerogen and clay decomposition are small. In fact, the standard errors of the equations used are greter than the difference.

Summary

In this report, we have developed three expressions for the heat of combustion of raw shale based on the composition of the shale. One-variable (wt % org C) and three-variable (wt % org C, S, acid CO_2) equations were developed from thermochemical considerations alone, and an additional one-variable expression was determined by linear regression. All work well, and the choice of which one to use depends on personal preference and the situation.

The heat-of-combustion formula for raw shale can be used in conjunction with other heat-of-combustion formulas to perform a heat balance on a shale pyrolysis. Such a calculation for Fischer assay products indicates that the heats of decomposition of kerogen and clays are small. We conclude with the reminder that we have considered combustion under conditions wherein standard state products such as SO_2 and $H_2O(l)$ are formed, and glass formation occurs. Heats from raw and retorted shale will be different under conditions where different mineral products are formed.

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Literature Cited

Burnham, A. K.; Crawford, P. C.; Carley, J. F. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 485.
Cambell, J. H. "Modified In Situ Retorting: Results from LLNL Pilot Retorting Experiments"; Lawrence Livermore Laboratory, UCRL-53168, 1981.
Cook, E. W. *Fuel* **1974**, 53, 16.
Ringen, S.; Lanum, J.; Miknis, F. P. *Fuel* **1979**, *58*, 69.
Singleton, M. F.; Koskinas, G. J.; Burnham, A. K.; Raley, J. H. "Assay Products from Green River Oil Shale"; Lawrence Livermore Laboratory, UCRL-53273, 1982.
Smith, J. W. "Ultimate Composition of Organic Material in Green River Oil Shale"; *U.S. Bur. Mines, Rept. Invest. 5725* **1961**.
Stanfield, K. E.; Frost, I. C.; McAuley, W. S.; Smith, H. N. "Properties of Colorado Oil Shale"; *U.S. Bur. Mines, Rept. Invest. 4825* **1951**.
Tripp, L. J. "L-3 Result Book"; Lawrence Livermore National Laboratory, Oil Shale Project, 1979.

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