

CALORIMETRIC DETERMINATION OF THE HEATS OF RETORTING
GREEN RIVER AND RUNDLE OIL SHALES TO 500°C AND OF
THE HEAT OF COMBUSTION OF SPENT GREEN RIVER SHALE AT 705°C

Stephen C. Mraw and Charles F. Keweshan

Exxon Research and Engineering Co.
Clinton Township, Annandale, New Jersey 08801

INTRODUCTION

Two important considerations for the future production of oil from shale are solids handling and heat management. For a resource yielding about 90 $\frac{\text{gal}}{\text{tonne}}$, two tonnes of rock must be handled for each barrel of oil produced, and large quantities of heat must be supplied or removed for the high-temperature processes involved. Proper reactor design and efficient process operations require accurate enthalpy data for retorting raw shale and combusting spent shale. It is part of our program in high-temperature calorimetry to develop novel techniques for oil-shale measurements and to provide accurate enthalpy data for shales of commercial interest. In previous papers, we have described a new method for determining the enthalpy of vaporization of organic materials at high temperatures (1), demonstrated the application of this method to oil-shale systems (2), and given a complete set of results for the heat of retorting raw Colorado Green River and Australian Rundle oil shales to 500°C (3). In the present paper we present new results for the heat of combustion of spent Green River shales at 705°C.

EXPERIMENTAL METHOD

Our apparatus is the high-temperature Calvet-type calorimeter described previously (4). Briefly, it consists of a central inconel block surrounded by a furnace designed for operation from room temperature to 1000°C. Within the block are two symmetrically mounted wells which serve as sample chambers. Each well is surrounded by a multi-junction thermopile which monitors the temperature difference between the well and the block. When any process within the sample chamber absorbs or liberates heat, the thermopile signal observed is proportional to the heat flow between the chamber and the block. The twin thermopiles are wired in opposition so that a difference reading is obtained for the left versus right sample chambers. A diagram of the apparatus is shown in Figure 1.

Most of the experiments to be described are "drop" experiments. A quartz or ceramic tube within the sample chamber is continuously swept with gas (nitrogen or oxygen, depending on the experiment), and a sample is dropped from room temperature into the receiving tube at the high temperature of the calorimeter. A peak in the thermopile signal records the total heat necessary to bring the sample from room temperature to its final state at high temperature. The area of the peak is directly proportional to the total heat.

[†] $\frac{\text{gal}}{\text{tonne}} = 4.174 \text{ U.S. gal/ton}$

In the case of samples dropped into nitrogen, we have developed a novel method for determining the heat necessary for rapid vaporization processes in the calorimeter (1). When a sample of an organic compound, or of a complex mixture, is dropped into the calorimeter at a temperature where evaporation or boiling is rapid, all processes can be completed within the time constant of the calorimeter (about 2 to 3 minutes). The calorimeter thermopile then responds "ballistically", and the peak height (as well as the more traditional peak area) is directly proportional to the total heat transferred to the sample. In Reference 2 we showed that the method was accurate beyond pure compounds and could be used to determine the heats associated with oil-shale processes. Results on Green River oil shale for the total enthalpy change



agreed very well with those from an earlier study using an entirely different technique (5).

In addition, this experiment for a complex material such as oil shale presents an opportunity to study the physical chemistry of the associated processes. When a sample is dropped into high temperature, some processes may be completed within the response time of the calorimeter, and other processes may take longer. The peak-height value will accurately represent the heat for the rapid processes, while the peak-area value will represent the total heat for all of the processes until the calorimeter returns to equilibrium (about 1.5 to 2.5 hours). Although comparison of the peak-height and peak-area values for each run nominally distinguishes rapid vs. slower processes, this can sometimes allow a distinction between organic and inorganic contributions. In Reference 3, we presented results for two complete sink-float series of raw shales, Colorado Green River and Australian Rundle. The enthalpy quantities for equation 1 were accurately determined, and the comparison of peak-height and peak-area values showed the importance of slower inorganic processes occurring in the Rundle shales at 500°C.

Calibration of the calorimetric sensitivity, both for endo- and exothermic events, is interspersed repeatedly among the actual shale experiments. For endothermic drops into nitrogen, the calorimetric sensitivity is determined by dropping samples of $\alpha\text{-Al}_2\text{O}_3$ into the calorimeter and recording both the height and area of the resulting peak. From the known enthalpy change (6) of Al_2O_3 between room temperature and the calorimeter temperature, both a peak-height and a peak-area calibration constant are calculated. For exothermic combustion experiments, the calorimetric sensitivity is determined using a calibration heater wound onto the ceramic tube which serves as the gas delivery inlet. A heat pulse is generated using a precision power supply, and the total heat is calculated from the known voltage and the measured resistance.

OIL-SHALE SAMPLES

The raw Green River oil-shale samples are from the sink-float separation procedures developed at Exxon Research and Engineering Company in Baytown, Texas (7). They are the same as those used in our retorting studies (3) and are from the Mahogany Zone (Colony Mine), ranging from 87 to 340 μ /tonne (21 to 82 U.S. gal/ton) Fischer Assay. Compositional details, includ-

ing mineral analyses, have been given by Vadovic (7). The powdered shale samples were dried in our laboratory over a P_2O_5 desiccant to remove surface moisture and loosely held water. Occasional checks have indicated that this process removes an amount of water comparable to that removed by drying at 105°C.

COMBUSTION OF SPENT GREEN RIVER SHALE AT 705°C

Combustion of Model Carbonaceous Materials

The electrical calibration procedure outlined earlier determines the calibration constant for the relatively "sterile" procedure of a controlled electrical power input within the thermopile reaction zone. To determine whether this constant is applicable to a vigorously combusting organic sample at high temperature, we performed several chemical checks using model combustions.

At 750°C, we measured the heat of combustion of SP-1 graphite (8). In our first experiments, using dry oxygen, the heat of combustion values were widely scattered and invariably low with respect to the literature value for graphite (9). We suspected incomplete combustion of carbon monoxide, and, when we humidified the oxygen by bubbling it through liquid water at room temperature (10), the combustion values immediately improved to within 3 to 4 percent of the literature value. By adjusting the gas flow rate to change the residence time of gases in the reaction zone, we eventually obtained an accuracy of 1 to 2 percent. Thus, all subsequent combustions of shale samples used humidified oxygen at a flow rate of 20 cm³/min. Further tests, both at 705 and 750°C, were made by combusting the highly-porous amorphous carbon, spherocarb (11), to simulate the rapid burning of a spent shale sample, and these tests indicated that the electrical calibration constant, even when applied to a rapid combustion, gives the true enthalpy value within a few percent.

To test whether volatile materials would combust within the thermopile zone under our conditions, we dropped samples of heavy, pure aromatic compounds directly into the oxygen stream in the calorimeter at 705°C. We used 1,2,5,6-dibenzanthracene ($t_{bp} = 524^\circ\text{C}$) and coronene ($t_{bp} = 525^\circ\text{C}$), and sample sizes (about 2 to 3 mg) were chosen to simulate the amount of organic that might volatilize from a spent shale sample. Even though combustion was not complete (60 to 90 percent of the expected enthalpy), we concluded that, if our system was this efficient in combusting these refractory molecules, we could expect volatile materials evolving from a spent shale to be combusted as well.

Preparation of Spent Shales

Pellets of each raw shale were pyrolyzed in a thermogravimetric analyser (TGA) to 500°C at heating rates of 50 to 100°C/min and held for 20 minutes. Most of the pellets could be recovered intact from the TGA and used for subsequent experiments. For pellets of the two richest samples, however, there was considerable swelling and cracking, often causing mechanical loss of some of the material. These pellets had to be held in gold crucibles during the TGA runs and in subsequent calorimetry experiments. To check that the TGA purge gas was reasonably free of oxygen, occasional samples were

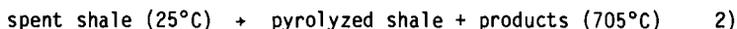
held at 500°C for periods of 40 minutes to four hours. There was no detectable mass change during these time periods. When the subsequent heat of combustion was compared to that of samples held for only 20 minutes, no loss of heating value was observed, indicating that no serious sample oxidation had occurred.

For each raw shale in the series, several pellets (approximately 30 to 100 mg each) were pyrolyzed in the TGA. Some were saved for calorimetric experiments, while, in general, two of each member of the series were sent for analysis (12). The resulting analyses are given in Table 1 and were used to calculate the amount of organic and inorganic material in each sample. However, the amount of Ca plus Mg, if assumed to be exclusively due to the minerals calcite, CaCO_3 , and dolomite, $\text{CaMg}(\text{CO}_3)_2$, predicts carbonate contents higher than those from the acid CO_2 tests. To arrive at a value for CO_2 content, we eventually took the simple average of the two possibilities for each sample. The inorganic carbon was then calculated and subtracted from the total carbon to yield the organic carbon value.

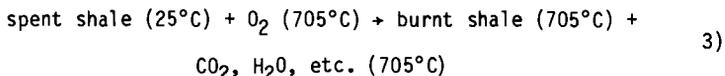
Spent Shale Experiments and Results

Using the 30 to 100 mg pellets described above, several experiments were performed on each spent shale at 705°C. This temperature was chosen because organic combustion is rapid, while carbonate decomposition is slow (13), giving us an opportunity to partially separate the heat effects.

In one set of experiments, the calorimeter sample chamber was continuously swept with nitrogen at flow rates ranging from 115 to 210 cm^3/min , and samples were dropped from room temperature into 705°C. From the endothermic peak in the thermopile signal, a peak-height and a peak-area enthalpy value were calculated for the process



Because of the slow carbonate decomposition, a long tail is evident on the peak, and there is a considerable difference between the peak-height and peak-area enthalpies (see below, Figure 2). In separate experiments, samples of spent shale were also dropped directly into the humidified oxygen stream (20 cm^2/min) to determine the total enthalpy

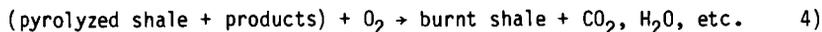


A typical thermopile signal showed a number of events. It first moved in the endothermic direction to record sensible heat but then quickly changed to the exothermic direction to record rapid combustion. Finally, it returned endothermic to continue recording slow carbonate decomposition. The character of the signal depends on the balance between organic material and carbonate minerals in the sample. For peaks of this type, the peak-height value is meaningless, and the area from initial to final baselines was used to calculate the enthalpy.

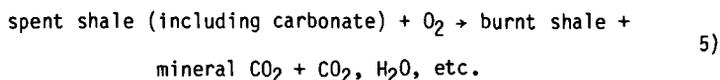
Figure 2 shows all of the experimental results from the nitrogen experiments (height and area) and from the oxygen experiments (area only), plotted vs. the percent organic carbon on the spent shale samples.

Experimental Heat of Combustion and Comparison to Literature

When the peak-area value from the nitrogen drop (Equation 2) is subtracted from that of the oxygen drop (Equation 3) the result is the heat of combustion of spent shale at 705°C, including shale volatiles:



We assume that all processes which occur under nitrogen also occur to the same extent under oxygen and that the combustion is then an additive contribution. In particular, both the carbonate decomposition enthalpy and any enthalpy of producing volatiles from the spent shale cancel in the subtraction. The enthalpy of volatiles production is expected to be small, and the carbonate decomposition enthalpy can be added back to give an adjusted form of Equation 4:



The experimental combustion values for Equation 5 are given in Table 2, where they are compared to literature values derived as follows.

Burnham *et al.* (14) report a correlation which represents the heats of combustion of spent Green River oil shales as determined by classical bomb combustion calorimetry. Since these heats refer to a set of specified standard states which are not typical of those expected at high temperatures, they adjust their correlation and give the following (their Equation 4) for the heat of combustion expected at high temperatures

$$\Delta H \text{ (J/g)} = -375.3 (\% \text{ organic C}) - 512.5 (\% \text{S}) + 20.85 (\% \text{CO}_2) \quad 6)$$

We have adjusted this further to change the final state for water from liquid to gas (by changing the term for % organic C from -375.3 to -368.0 as they recommend) and to change the final state for nitrogen from N₂ to a mixture of NO and NO₂. The resulting equation then assumes that the following processes occur: combustion of organic material, combustion of organic sulfur and inorganic sulfides, capture of SO₂ as sulfates, and decomposition of carbonates. However, one important question concerning the combustions at 705°C in our calorimeter is whether calcium and magnesium oxides have reacted with SiO₂ to form new silicate compounds. Literature indicates that the rates of these reactions are enhanced by steam (13), but we do not know whether the low level of moisture in our oxygen is enough to have a significant effect. Thus, in Table 2 we have calculated "literature" values in two ways, assuming either no silicate formation or complete silicate formation, using the terms given by Burnham *et al.* (14).

In Table 2, the overall agreement between our new data and the literature values, even toward the richer fractions, shows that to first order the heat of combustion at high temperatures is understood fairly well. However, as Burnham *et al.* (14) also concluded (concerning their bomb calorimetry

results), there are important questions remaining, particularly on the role of mineral reactions. For example, the experimental scatter does not permit a definitive statement on the occurrence of silicate reactions in our calorimeter, since some of the points in Table 2 support one assumption and some the other.

CONCLUSION

High-temperature Calvet calorimetry is a powerful means of determining accurate enthalpy values for oil shale processes at high temperatures, using very small samples (50 to 200 mg). By using samples from sink-float separation procedures (7), a wide range of organic and inorganic contributions can be studied. In a previous paper (3), values for the heat of retorting Green River oil shales to 500°C have been extended beyond the oil yields previously studied (5,15), and the first accurate values for Rundle shales were determined. To our knowledge, the present study also represents the first attempt to measure heats of combustion of spent shales in a high-temperature calorimeter (i.e. other than by differential scanning calorimetry or differential thermal analysis). Results for spent Green River oil shales at 705°C agree reasonably well with those derived from classical bomb calorimetry, but there are important questions remaining on the contributions of mineral reactions to the enthalpy.

ACKNOWLEDGEMENT

We thank Charles J. Vadovic for providing us with the valuable series of sink-float samples and the many colleagues at Exxon who have offered valuable comments and suggestions during the course of this work.

REFERENCES

1. Mraw, S. C.; Keweshan, C. F. J. Chem. Thermodynamics 1984, 16, 873.
2. Mraw, S. C.; Keweshan, C. F. Ind. Eng. Chem., Fundamentals 1985, in press. (See also, AIChE Spring National Meeting, May 20-23, 1984, Anaheim, California, USA.)
3. Mraw, S. C.; Keweshan, C. F., paper submitted to Fuel.
4. Mraw, S. C.; Kleppa, O. J. J. Chem. Thermodynamics 1984, 16, 865.
5. Wise, R. L.; Miller, R. C.; Sohns, H. W., U.S. Bureau of Mines, 1971, Report of Investigation 7482.
6. JANAF Thermochemical Tables. Stull, D. R.; Prophet, H., directors. 2nd ed. NSRDS-NBS 37: U.S. Government Printing Office, Washington, DC 1971.
7. Vadovic, C. J. Prepr. Am. Chem. Soc. Div. Fuel. Chem. 1983, 28(3), 148.
8. Union Carbide Corporation, Carbon Products Division, New York, New York.
9. Stull, D. R.; Westrum; E. F., Jr.; Sinke, G. C., The Chemical Thermodynamics of Organic Compounds, Wiley: New York, 1969.
10. We thank James E. Hardy of this laboratory for this valuable suggestion.
11. Analabs, Inc., 80 Republic Dr., North Haven, Connecticut 06473.
12. Galbraith Laboratories, Inc., P. O. Box 4187, Knoxville, TN 37921.
13. Burnham, A. K.; Stubblefield, C. T.; Campbell, J. H. Fuel 1980, 59, 871.
14. Burnham, A. K.; Crawford, P. C.; Carley, J. F. Ind. Eng. Chem. Process Des. Dev. 1982, 21, 485.
15. Carley, J. F., Lawrence Livermore National Laboratory, private communication, to be published.

Table 1

Analyses of Green River Shale Samples Retorted by TGA to 500°C
(Galbraith Laboratories (12))

Sample	C (total)	% of dried spent shale					ash	carbonate C	SO ₃ (% on ash)
		H	N	S	Ca	Mg			
2.2S	8.74	0.27	0.29	0.81	16.60	3.96	74.75	6.64	2.80
2.2F	9.48	0.28	0.33	0.70	17.74	4.03	74.27	6.53	2.89
2.0F	9.54	0.32	0.42	0.98	14.97	4.06	75.73	5.76	3.20
1.9F	10.24	0.45	0.65	1.36	10.89	3.96	78.03	4.52	4.89
1.8F	11.19	0.56	0.71	1.60	9.63	3.71	77.36	4.13	5.74
1.7F	12.16	0.59	0.80	2.06	8.60	3.36	78.13	3.76	7.04
1.6F	12.10	0.61	0.79	2.34	8.62	2.66	78.82	3.19	6.57

Table 2

Experimental values, derived from the present work, for the heat of combustion of spent Green River oil shale at 705°C, and comparison to values derived from bomb calorimetry (14); see text.

sample	organic C (% spent shale)	-ΔH _c (kJ/g of spent shale)		
		this work ^a	Reference 14	
			w/o silicates	w silicates
2.2S	1.96	0.34 ± 0.05	0.22	0.59
2.2F	2.56	0.79 ± 0.14	0.36	0.75
2.0F	3.42	1.15 ± 0.06	0.93	1.26
1.9F	5.37	2.26 ± 0.06	2.01	2.26
1.8F	6.77	2.57 ± 0.11	2.71	2.92
1.7F	8.16	3.37 ± 0.07	3.51	3.69
1.6F	8.56	3.77 ± 0.06	3.86	4.00

^aValues given for each sample represent the average peak-area enthalpy from the oxygen drops minus that from the nitrogen drops and then adjusted to include carbonate decomposition, according to Equation 5 in the text.

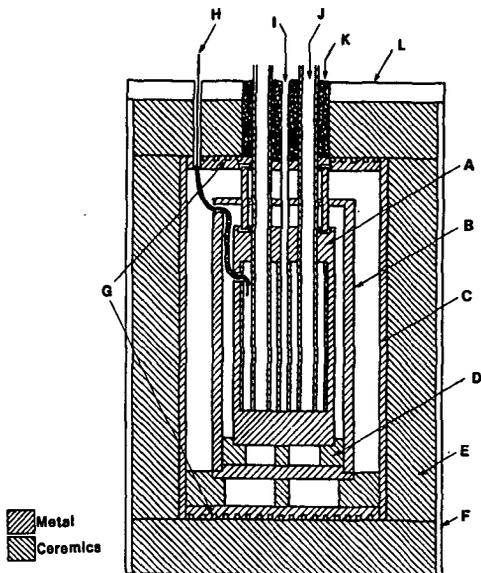


Figure 1

Assembly diagram of the high-temperature calorimeter (overall dimensions: $h=80$ cm; $d=65$ cm). A: Inconel block; B: temperature homogenizing shield; C: furnace shell; D: ceramic support blocks; E: cast refractory insulation; F: side water jacket; G: grooves for top and bottom heater wires; H: typical thermopile lead wire; I: central well for precision thermocouple; J: ceramic tube sample chamber; K: ceramic wool; L: top water jacket.

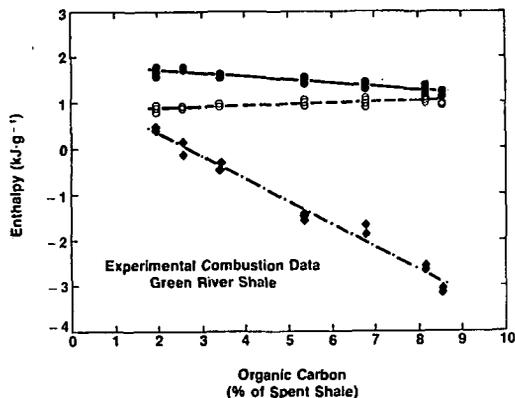


Figure 2

Experimental enthalpy values determined from drops of spent Green River shale into nitrogen or oxygen at 705°C , vs. the percent organic carbon on spent shale.

○, --- nitrogen peak height
 ●, — nitrogen peak area
 ◆, - - - oxygen peak area