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COMBUSTION CALORIMETRY OF OIL SHALES *

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ABSTRACT

Samples of raw oil shale and spent shale from combustion-retorting experiments are burned in a calorimeter to determine their heats of combustion. The shales are mixed with an equal amount of benzoic acid to achieve complete combustion A platinum crucible with a basket is used to allow minimal contact of sample with platinum This design reduces quenching effects by permitting oxygen to completely surround the sample. The heats of combustion, $-\Delta H_c$, for raw shale range from 1150 to 1250 cal g^{-1} while those for spent shale range from —65 to —15 cal g^{-1}. The precision of the analysis gives a standard deviation of approximately 5 cal g^{-1}. Uncertainties in the sulfur correction and the gas correction, Δn, have the largest effect on the accuracy of the analysis

INTRODUCTION

Oil shale from the Anvil Points mine in Colorado has been combustion-retorted in a number of experiments directed toward development of modified in-situ retorting [1]. To determine the energy balance in these experiments, the heating values of the raw shale and of the products — oil, spent shale, and gas — must be known. The heating values of the gaseous products are calculated, while the heating values of the raw shale, spent shale, and oil are determined by measuring their heats of combustion by bomb calorimetry. In this paper, the heats of combustion of raw and spent oil shale are reported, and the procedures employed are described.

EXPERIMENTAL

The raw shale is crushed, riffled, and split before retorting. A portion of the batch to be retorted is further ground and split for analytical purposes. All of the spent shale is ground, mixed, and split after the experiment is

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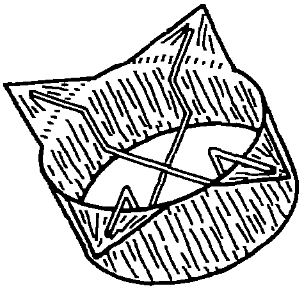

Fig. 1. Platinum basket and cup

completed. Therefore, the samples received for analysis are assumed to be representative.

Portions of the pelleted shale remained unburned after trial combustions. To achieve complete combustion, it is necessary to further grind the samples and also to mix them with benzoic acid [2]. The shales are ground for 2 min in a Bleuler mill to achieve a particle size of <43 μm for 95% of the material. The benzoic acid is ground to a particle size of <124 μm. Shale and benzoic acid are mixed in a 1 : 1 ratio and pelleted before combustion.

Trial samples were burned in a platinum crucible. Observation of the residue after combustion showed traces of unburned sample where the sample was in contact with the platinum. Therefore, a crucible was designed that has a basket made of 0.75 mm (30 mil) platinum wire. The wire is arc-welded to a cup made of 25 μm (1 mil) platinum foil (see Fig. 1). The cup is approximately 25 mm in diameter and 15 mm high. There is approximately a 5 mm clearance between the bottom of the crucible and the bottom of the basket to allow oxygen to surround the sample pellet.

The heats of combustion are determined by using an isothermally jacketed, Parr * bomb calorimeter. The bomb contains 3.04 MPa (30 atm) oxygen. Temperatures are measured with a Hewlett Packard Model 2810A quartz thermometer that is interfaced to a Digital Computer Controls, Inc., D-112 computer [3]. Temperatures are read every 10.5 sec. The computer program checks the foredrift for linearity, activates the firing relay, terminates the experiment when complete, and calculates the corrected temperature rise [4]. Once this value is obtained, the gross calorific value [5] at constant volume, $-\Delta E$, and the heat of combustion at constant pressure, $-\Delta H_c$, are calculated.

RESULTS

Duplicate or triplicate combustion analyses are made on each sample. Typical results are shown in Table 1. The calorimeter is calibrated using a certified benzoic acid standard ($-\Delta H_c = 6319$ cal g^{-1}). The reagent-grade

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* Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U S. Department of Energy to the exclusion of others that may be suitable

TABLE 1

Combustion analyses (298 K, $H_2O_{(l)}$, CO_2, N_2, SO_2)

Material	$-\Delta H_c$ (cal g^{-1})				Estimated standard deviation
	Run 1	Run 2	Run 3	Ave	
Benzoic acid	6312.6	6316 4	6317 2	6315.4	2.7
Raw shale					
I	1208.9	1206.0	1212.0	1209.0	3.5
II	1213.9	1214.4	1208.2	1212.2	3.7
Spent shale					
I	−65.5	−62.0	−69.6	−65.7	4.5
II	−14.2	−19.9	−12.1	−15.4	4.6

benzoic acid reported is ground and mixed with the shale samples. The spent shales give negative $-\Delta H$ values, indicating an endothermic process.

DISCUSSION

The tabulated heats of combustion of benzoic acid, raw shale, and spent shale vary in magnitude. However, in each case the estimated standard deviation for three runs is less than 5 cal g^{-1}, which gives confidence in the precision of our measurements.

Several sources of error can affect the accuracy of the results. These are due to inhomogeneity of the sample, losses during mixing and transferring operations, and uncertainties in the sulfur correction and in the correction for Δn, the change in moles of gas in the bomb.

There is always a problem in preparing representative and homogeneous analytical samples of inhomogeneous materials like oil shale. The precision of our results indicates the samples are well prepared, and we assume they are representative of the entire charge of shale.

A probability of error exists in mixing and transferring operations. The shale and benzoic acid are carefully weighed into a mixing bottle. After mixing, they are transferred to a mechanical die for pressing into a pellet. Some sample material is lost during this operation. The sample pellet is weighed, and the amounts of shale and benzoic acid are calculated from the ratio of the original individual weights. If the amounts of the individual components lost were not proportional, errors would arise because of the different heats of combustion of oil shale and benzoic acid. However, the precision of the analysis indicates this is not a significant problem.

Chemical analysis of sulfur in raw shale shows 67% is present as sulfides, 33% as organic sulfur, and trace amounts as sulfates [6]. The sulfur in spent shale is present primarily as sulfides, with traces of sulfates. This analysis is assumed to represent the sulfur distribution in the shales used in this study. During combustion, sulfur reacts with oxygen to form SO_2. One atmosphere of air is left in the bomb when the oxygen is added. Nitrogen oxides formed from the air nitrogen oxidize the SO_2 to SO_3, which dissolves in the water present and forms sulfuric acid. Total acid in the bomb wash is determined by titration with NaOH, and nitrate is determined by using an ion-selective electrode. Sulfate is determined by the difference. Using these values for nitrate and sulfate, corrections are made to the standard states, N_2 and SO_2.

There are several sources of error in this procedure. The sulfur may not be quantitatively converted to SO_2. The SO_2 may not all be converted to SO_3. The bomb is not rotated to wash the surfaces during combustion so formation of sulfuric acid may be incomplete. The method used to determine the sulfate concentration has inaccuracies. The percent of sulfur in the samples is low, resulting in corrections of 3—15 cal g^{-1}.

A correction must be made to compensate for the change in moles of gas, Δn, in the calorimeter during combustion. The following assumptions are made. Carbon (mineral) is present as carbonates, which decompose forming oxides and liberating CO_2 ($\Delta n = +$). Organic carbon and sulfur combine with oxygen to form CO_2 and SO_2 ($\Delta n = 0$). Organic hydrogen combines with oxygen to form water ($\Delta n = —$). The samples are analyzed for organic hydrogen and acid CO_2. Using these values and the ideal gas law, corrections for the estimated changes in pressure are calculated. The corrections are of the order of 2—4 cal g^{-1}.

In the energy balance calculations, the raw and spent shale are assumed to go to the same final products. No attempt is made to compare the gaseous products. The solid residues from a raw and a spent shale were compared. The residues are large, greenish-black, glossy globules, which flow around the bottom wires of the platinum basket. Some droplets are found in the platinum cup. Visually, residues from both sources appear identical. X-ray diffraction studies show both samples are amorphous. X-ray fluorescence analysis shows the same approximate relative elemental concentrations by weight. No differences are observed in IR spectra. We conclude the assumption is justified that the same final products are formed in combustion of raw and spent shales.

For the energy balance calculations, it is important that the temperatures in the calorimeter bomb be above those in the combustion retort. There is evidence of melting of platinum wire in the bomb during the experiment, which indicates temperatures as high as 2042 K. The highest temperatures reached in the combustion retort experiments are approximately 1275 K.

CONCLUSION

In determining the heats of combustion of oil shales, it is necessary to mix the shale samples with benzoic acid and to use a sample holder that allows oxygen to surround the sample pellet. Results obtained with these techniques show good precision with an estimated standard deviation of 5 cal g^{-1}. These results are used in energy-balance calculations in oil-shale retorting experiments.

REFERENCES

1 J H. Raley, W.A. Sandholtz and F J Ackerman, Proceedings of the Twelfth Oil Shale Symposium, Colorado School of Mines, Golden, Colo , 1978.
2 L. Dockter, U.S. Bureau of Mines, Laramie, Wyo., private communication, 18 March 1976.
3 E. Catalano and J C. English, Anal. Calorim., 3 (1974) 69.
4 F.D Rossini, Experimental Thermochemistry, Interscience, New York, 1956, pp 28—32
5 ASTM D 3286-73, in 1977 Annual Book of ASTM Standards, Part 26, American Society for Testing Materials, Philadelphia, Pa., pp. 402—410.
6 Synthetic Fuels Data Handbook, Cameron Engineers, Inc , Denver, Colo , 1975, pp 38, 40.