

THE HEAT OF REACTION OF ³⁹³HYDROGEN AND COAL

A. L. Lee, H. L. Feldkirchner, F. C. Schora, and J. J. Henry*

Institute of Gas Technology
Chicago, Illinois

INTRODUCTION

This investigation is a part of the study conducted at the Institute of Gas Technology (1,2,4,5,6,7,9,10,11) to obtain the necessary information for designing an efficient coal hydrogasification plant. A thorough literature search reveals that there is no reported data on the heat of reaction of hydrogen and coal. Therefore, two calorimeters were designed, constructed, and operated, one to measure the heat of reaction and the other to measure heat capacity by the drop method. The heat-of-reaction calorimeter can be operated at temperatures up to 1500°F and pressures up to 1500 psia; the drop calorimeter operates at atmospheric pressure and temperatures up to 1500°F. This paper reports the results of the following investigations:

1. The heat of reaction of hydrogen with coals and coal chars after various degrees of gasification.
2. The heat of reaction of coal pretreatment.
3. The heat capacity of coals and coal chars.

APPARATUS

The heat-of-reaction calorimeter built by Dynatech Corporation is shown in Figure 1. The sample is placed in the upper portion of the neck which is cold. The calorimeter body is filled with hydrogen and heated. The temperature of the calorimeter body is measured by four thermocouples and two platinum resistance thermometers. The sample is lowered into the body after the temperature has remained steady for 2 hours. The change in temperature due to a reaction is then measured as a function of time.

The drop calorimeter, which was also built by Dynatech, is shown in Figure 2. The sample is placed in the top furnace until it reaches the desired temperature. It is then dropped into the copper receiver, and the heat capacity of the sample is determined from the temperature rise and heat capacity of the copper receiver.

EXPERIMENTAL RESULTS

The major problem encountered in determining the heat of coal reactions at high temperature and high pressure is prereaction, since coals decompose when heated. Meaningful results can be obtained only if the coal and hydrogen react at conditions at which the desired temperature and pressure are stabilized. Therefore, the method of introducing the sample to the reaction conditions is critical. The coal must not react before the conditions are set, and the pressure must not be disturbed when the coal is introduced.

* Dynatech Corp., Cambridge, Massachusetts.

The present method is to keep the sample at room temperature inside the calorimeter drop tube so that the reaction will not take place prematurely. Convection shields are installed to prevent a large heat loss from convection and to ensure that the sample is in a cold zone while the calorimeter is being stabilized at the reaction conditions.

Establishing a heat balance around the calorimeter was necessary in order to calculate the heat of reaction from experimental data. The heat balance is best expressed by:

$$\Delta\bar{H}_R + h_{in} = (mC_p\Delta T)_{\text{calorimeter}} + (mC_p\Delta T)_{\text{shield}} + (mC_p\Delta T)_{\text{chain}} + (mC_p\Delta T)_{\text{basket}} + (mC_p\Delta T)_{\text{coal}} \quad (1)$$

where: $\Delta\bar{H}_R$ = heat of reaction
 h_{in} = heat input from the neck heater
 m = mass
 C_p = heat capacity
 ΔT = temperature change

Each term in Equation 1 must be either established by calibration or accurately measured. The heat capacity of the calorimeter metal was determined in the drop calorimeter. These data are shown in Figure 3.

The effective mC_p of the reaction calorimeter was calibrated by a constant-heat-input technique in a hydrogen atmosphere at 1000 psia and temperatures from 840° to 1460°F. The results are presented in Figure 4. After the calorimeter constants were determined, the effective $(mC_p\Delta T)$'s of the convection shield, the chain, and the empty sample basket were calibrated in the calorimeter to determine the change of heat input with time, as shown in Equation 2:

$$K(\theta) = \int_0^{\theta} (mC_p\Delta T)_{\text{empty calorimeter}} d\theta = \int_0^{\theta} [(h_{in} - (mC_p\Delta T)_{\text{shield}} - (mC_p\Delta T)_{\text{chain}} - (mC_p\Delta T)_{\text{basket}})] d\theta \quad (2)$$

where: $K(\theta)$ = a constant dependent only on time
 θ = time

Combining Equations 1 and 2, we have:

$$\Delta\bar{H}_R = (mC_p\Delta T)_{\text{calorimeter}} + (mC_p\Delta T)_{\text{coal}} - K(\theta) \quad (3)$$

Equation 3 was used to calculate the heat-of-reaction data reported in this paper.

Design of a hydrogasification plant requires data on the heats of reaction of raw coal in the coal pretreatment process, the pretreated coal in the low-temperature gasifier, the residue from the low-temperature gasifier in the high-temperature gasifier, and the residue from the high-temperature gasifier (4,6). The heat-of-reaction and heat capacity measurements are given in Tables 1 and 2. Figure 5 shows the temperature and pressure profiles of a typical experimental run.

DISCUSSION

Until now, the heat of the coal hydrogasification reaction has only been determined by calculation. These calculations have become more precise as more data became available, but no measurements were made to check the validity of the calculated data.

Initially (in the absence of accurate pilot plant yield data), the heat of reaction was estimated by assuming that coal and carbon were equivalent and that the hydrogasification reaction could be approximated by (5,8):



This approach, of course, is very crude and could not be expected to give a reliable answer, but it could be useful for comparing the thermal efficiencies of various gasification processes.

The next approach, using pilot plant data (7), was to calculate the heat of reaction from the heats of combustion of the reactants and products. The heats of combustion of various coals could be obtained by a Parr-bomb calorimeter or calculated by the modified Dulong formula. But if one attempts to calculate the heat of reaction of hydrogen and coal from heats of combustion, there are two drawbacks. First, because the calculation involves taking the differences of large numbers of the same order of magnitude, chemical analyses of all reactants and products must be very accurate and pilot material balances must be quite close to 100 percent or else the balance must be forced. If this is not the case, large errors can be made in this calculation. This makes the calculated heat of reaction dependent on the quality of the analytical data and on the method used to force the balance. The second drawback is that the calculated heat of reaction is determined for 25°C, so no information is obtained on the reaction heat at actual reaction temperatures.

Of course, if the heat of reaction could be determined at one temperature, the heat of reaction at various temperatures could be calculated from heat capacity data. Some heat capacity data are available in the literature for coals and cokes, but none are available for the particular coals used here. Moreover, the measurement methods used so far are not very accurate. In most cases the gaseous decomposition products were allowed to escape from the calorimeters during coal heatup, and, consequently, the heat capacity data are rather doubtful.

A comparison of the heats of reaction of hydrogen and coal obtained from the heat of formation data for $C + 2H_2 \rightarrow CH_4$ and the pilot plant data with that obtained from the calorimetry studies is shown in Figure 6. Note that the pilot plant data were based on a 77°F reference

temperature, while the present experimental data were obtained at operating conditions. Moreover, the experimental data were obtained from coals at four different stages of reaction: raw coal, pretreated coal, low-temperature gasification residue, and high-temperature gasification residue. Ash balances were used to put these results on a common basis. The ash balance calculations gave the percent of carbon gasified in each coal or char. Raw coal was assumed to have 0% carbon gasified. Thus Figure 6 shows the general trend of the heat of reaction.

Accurate heat-of-reaction data are given in Table 1. Although the pilot plant data are considerably scattered, the average value is not too different from that obtained by the other methods. The calorimetry data also show some scattering, which is due to the heterogeneous nature of the coal, and the characteristics of the calorimeter and the sensing instruments. Examinations of the temperature measurement, the pressure measurement, the temperature distribution in the calorimeter, the total mass balance, and the calibration results obtained from the constant-heat-input method and experimental runs on hydrogen and n-decane reactions indicate that the data reported in Table 2 should not have a deviation greater than 10%.

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1. Feldkirchner, H. L. and Huebler, J., "Reaction of Coal With Steam-Hydrogen Mixtures at High Temperatures and Pressures," Ind. Eng. Chem. Process Design Develop. 4, 134-42 (1965) April.
2. Huebler, J. and Schora, F. C., "Coal Hydrogasification," Chem. Eng. Progr. 62, 87-91 (1966) February.
3. JANAF Thermochemical Tables. Distributed by: Clearinghouse for Federal Scientific and Technical Information, Springfield, Va.
4. Kavlick, V. J. and Lee, B. S., "Coal Pretreatment in Fluidized Bed," Amer. Chem. Soc. Div. Fuel Chem. Preprints 10, No. 4, 131-39 (1966) September.
5. Linden, H. R., "Pipeline Gas From Coal: Status and Future Prospects," Coal Age 71, 64-71 (1966) January.
6. Pyrcioch, E. J., Lee, B. S. and Schora, F. C., "Hydrogasification of Pretreated Coal for Pipeline Gas Production," Amer. Chem. Soc. Div. Fuel Chem. Preprints 10, No. 4, 206-23 (1966) September.
7. Pyrcioch, E. J. and Linden, H. R., "Pipeline Gas by High-Pressure Fluid-Bed Hydrogasification of Char," Ind. Eng. Chem. 52, 590-94 (1960) July.
8. Rossini, F. D. et al., Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds. Pittsburgh: Carnegie Press, 1953.
9. Tajbl, D. G., Feldkirchner, H. L. and Lee, A. L., "Cleanup Methanation for Hydrogasification Process," Amer. Chem. Soc. Div. Fuel Chem. Preprints 10, No. 4, 235-45 (1966) September.
10. Tsaros, C. L. and Feldkirchner, H. L., "Production of High Btu Gas," Chem. Eng. Progr. 62, 49-54 (1966) August.
11. von Fredersdorff, C. G. and Vandaveer, F. E., "Substitute Natural Gas From Coal," in Segeler, C. G., Ed., Gas Engineers Handbook, Section 3, Chap. 9, 3/100-3/123. New York: The Industrial Press, 1965.

Table 1. ANALYSIS OF COAL AND COAL CHARS

	<u>Raw Coal</u>	<u>Pretreated Coal</u>	<u>Low-Temp Residue</u>	<u>High-Temp Residue</u>
Proximate Analysis, wt %				
Moisture	1.3	0.5	0.6	0.6
Volatiles	34.6	23.3	4.6	3.3
Fixed Carbon	52.0	63.5	77.6	71.6
Ash	12.1	12.7	17.2	24.5
Total	100.0	100.0	100.0	100.0
Ultimate Analysis, wt %				
Carbon	71.2	70.1	76.9	72.6
Hydrogen	5.14	3.70	2.05	1.08
Nitrogen	1.23	1.37	1.01	0.54
Oxygen	6.03	8.30	0.65	0.00
Sulfur	4.19	3.80	2.09	1.24
Ash	12.21	12.73	17.30	24.62
Total	100.00	100.00	100.00	100.00
Reaction Temperature, °F	1300	1300	1300	1300
Reaction Pressure, psia	1000	1000	1000	1000
Coal Reacted (Avg), %	49.7	47.2	27.3	28.8
Carbon Gasified (Avg), %	50.6	41.0	29.5	26.0
Avg ΔH_R , Btu/lb coal reacted	1817	1919	2432	3078

Table 2. HEAT OF REACTION OF COAL

<u>Material</u>	<u>Temperature, °F</u>	<u>Pressure, psia</u>	<u>Coal Reacted, %</u>	<u>Carbon Gasified, %</u>	<u>ΔH_R, Btu/lb coal reacted</u>
Raw coal	1000	1000	41.5	--	1300
Raw coal	1300	1000	52.4	50.7	1951
Raw coal	1300	1000	52.2	52.0	1723
Raw coal	1300	1000	48.1	55.6	1788
Raw coal	1300	1000	46.1	44.2	1807
Raw coal	1400	1000	51.7	52.3	1775
Pretreated coal	1300	1000	46.1	37.6	1935
Pretreated coal	1300	1000	47.3	41.2	1717
Pretreated coal	1300	1000	47.3	41.5	1844
Pretreated coal	1300	1000	47.1	40.0	2476
Pretreated coal	1300	1000	48.3	45.0	1625
Low-temp residue	1300	1000	27.3	29.5	2432
Low-temp residue	1300	1000	--	--	2566
High-temp residue	1300	1000	28.8	26.0	3078

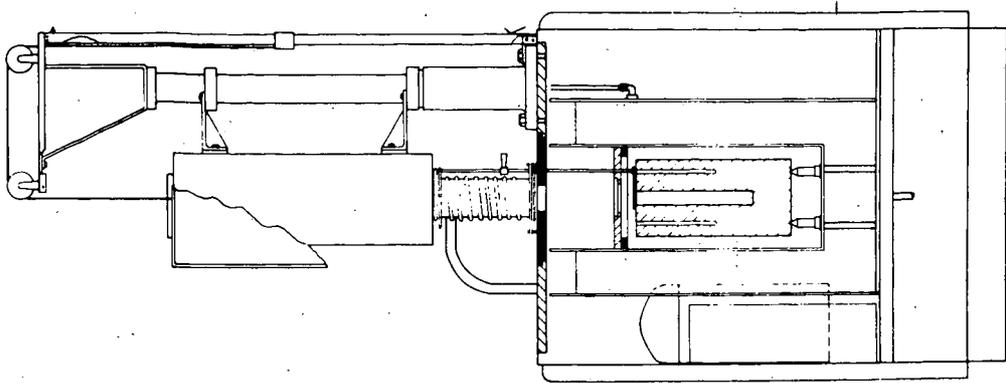


Figure 2. DROP CALORIMETER

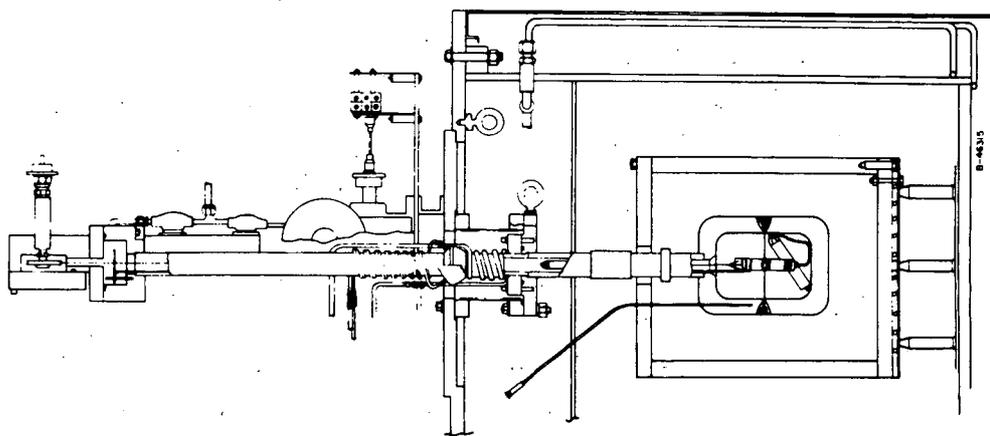


Figure 1. HEAT-OF-REACTION CALORIMETER

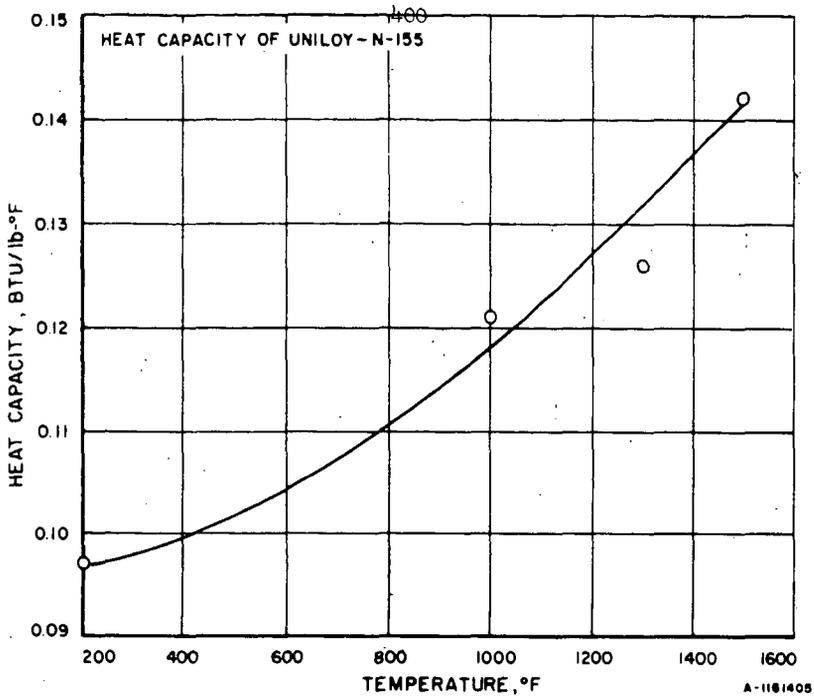


Figure 3. MEAN HEAT CAPACITY OF CALORIMETER
(From 70°F to Temperatures Indicated)

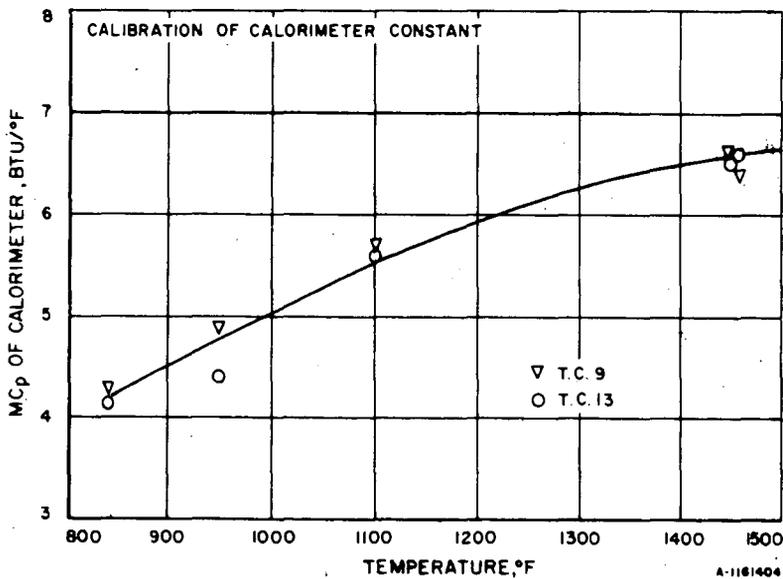


Figure 4. CALIBRATION OF HEAT-OF-REACTION CALORIMETER

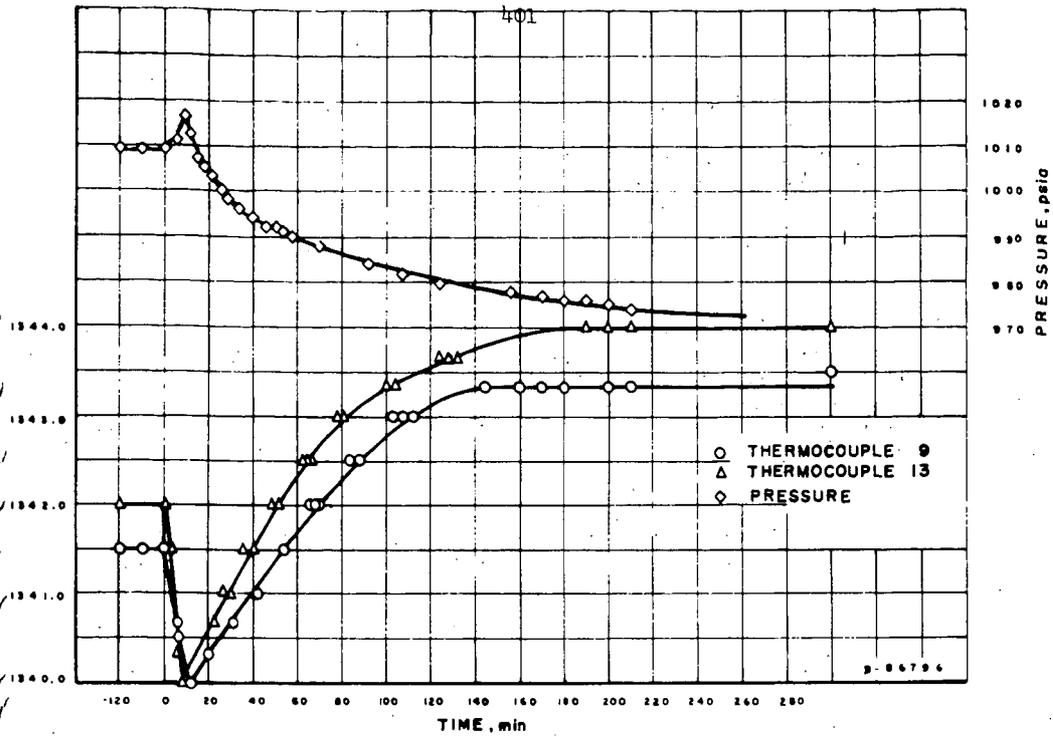


Figure 5. TIME-TEMPERATURE DATA FOR HEAT OF REACTION OF HYDROGEN AND COAL

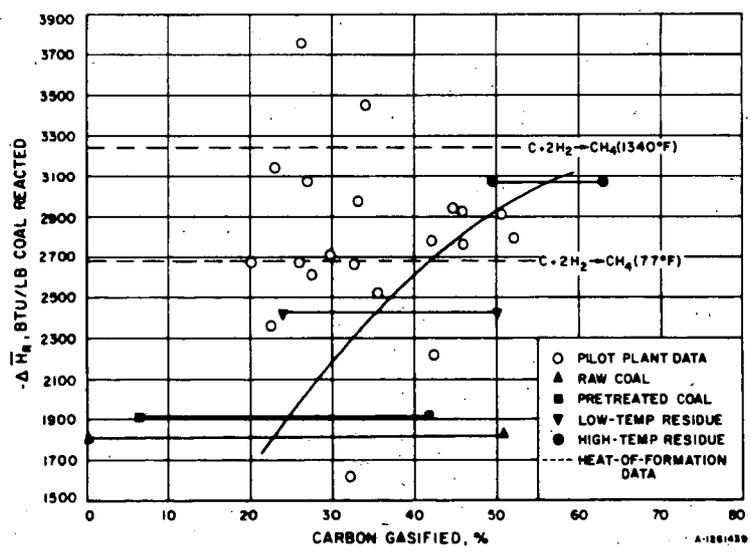


Figure 6. COMPARISON OF DATA FOR HEAT OF REACTION OF HYDROGEN AND COAL