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THERMOPHYSICAL PROPERTIES OF COAL LIQUIDS

Seventh Quarterly Technical Status Report for the Period April 1—June 30, 1981

By
J. W. Droege
R. Venkateswar
S. P. Chauhan

July 17, 1981

Work Performed Under Contract No. AC22-79ET14941

Battelle Columbus Laboratories
Columbus, Ohio

U. S. DEPARTMENT OF ENERGY

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SEVENTH QUARTERLY TECHNICAL STATUS REPORT

on

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COAL LIQUIDS

for the Period

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and S. P. Chauhan

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505 King Avenue
Columbus, Ohio 43201

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ABSTRACT

Measurements of rheological properties have been continued. Measurements at relatively low temperature (450 K) showed that a coarser coal grind shows substantially lower viscosity. It was also shown that coal and solvent obtained from the Fort Lewis plant gave slurries of much higher viscosity than slurries from our reference coal and solvent. At higher temperatures (540 K) substantially the same relationships were shown. The effect of solvent-to-coal ratio was also found to be very great.

Differential scanning calorimetry gave some low reliability specific heat results and showed indication of a probable heat effect at about 500 K. No indication of exothermic reaction with hydrogen was found.

OBJECTIVES AND SCOPE OF WORK

The objective of the project is the determination of thermophysical properties of reacting hydrogen-coal-solvent systems. The results are intended to show the changes in viscosity, density, thermal conductivity, and heat content as these slurries are heated to temperatures at which solvation takes place. To the extent possible, the time-temperature-pressure pattern in the preheater section of a liquefaction plant are duplicated.

In order to attain these objectives, the following eight tasks have been undertaken.

Task 1: Experimental Plan. The detailed plan for experiments to be performed is based on consultation with Air Products and Chemicals, Inc. (APCI), a subcontractor, and with others engaged in similar work. It includes a ranking of physical properties according to their importance in preheater design, a selection of a reference coal and reference solvent, and a listing of the most important variables to be studied.

Task 2: Sample Preparation and Analysis. Certain measurements require samples prepared in separate experiments. These are prepared by a short residence time technique. These samples, together with the starting materials, are subjected to careful analysis. Most of the experiments are conducted with mixtures of solvent and pulverized coal. The residues from these experiments are characterized by solvent extraction techniques.

Task 3: Rheology. A falling-cylinder viscometer is used to characterize the slurries. With this instrument it is possible to determine the shear stress as a function of shear rate. Measurements are made at constantly increasing temperature and at constant temperature.

Task 4: Thermal Conductivity. Measurements are made by a transient technique using a heated wire as a line source.

Task 5: Calorimetry. A pressurized differential scanning calorimeter (DSC) is used to find the energy change when samples undergo dissolution reactions. The apparatus and technique require modification to provide access of hydrogen to the sample while preventing evaporation. Specific heat is determined by DSC.

Task 6: Density. Samples are confined in vessels of known volume to determine density as a function of temperature. In some cases prior degassing is required.

Task 7: Interpretation. Results will be analyzed for their applicability to the preheater in a liquefaction plant. The bulk of this work will be done by APCI.

Task 8: Final Report. The report will include a complete description of the experiments together with the results and interpretation.

RESULTS THIS QUARTER

Task 3. Rheology

Measurements are being made in a reciprocating cylinder viscometer. A bob moves up and down in an autoclave, pumping the sample through the space between the bob and the wall. Force and rate of movement are measured. In order to initiate an experiment the slurry is transferred under pressure from a cold autoclave to the preheated viscometer so that constant temperature measurements can begin within a few minutes.

A variety of measurements were made during the past quarter. They include measurements on the reference coal and solvent, a KY-9 coal ground under protective atmosphere to -200 mesh and a Wilsonville recycle solvent. Some of these measurements were made at several solvent-to-coal ratios (S/C) in an effort to obtain data with dilute mixtures that could be extrapolated toward more concentrated mixtures. Some of the measurements were made at relatively low temperatures to obtain data relating to the mixing tank and heat exchanger. Some measurements were made on materials obtained from The Pittsburg and Midway Coal Mining Company in an attempt to reconcile apparent discrepancies. Some measurements were made with a coarser grind of coal to assess the significance of particle size on rheological behavior.

The quality of the data was variable. In some cases satisfactory, reproducible data were obtained. In some cases the data were so distorted or poorly reproducible that only qualitative results could be obtained. The difficulties were associated, as in the past, with samples which had thickened, presumably by swelling of coal particles and absorption of solvent. These mixtures contained both solids and liquids which easily separated.

In each case the data were plotted as a function of time, giving a series of smooth curves at constant lifting force. Cross plots were then prepared, showing peak heights in millivolts as a function of force applied. A series of such plots represented the changing behavior of the sample. From the slopes of these straight lines, using calibration data obtained with standard oils, values of plastic viscosity were obtained.

The force required to balance the bob in the slurry was calculated from the known volume of the bob and density of the slurry. From this calculated value and from the observed intercepts of the straight line, the yield stress was obtained. Thus, the data are represented by the equation:

$$\tau = \tau_o + \eta_{pl} \dot{\gamma}, \quad (1)$$

where

τ = The shear stress

τ_o = The yield stress

η_{pl} = The plastic viscosity

$\dot{\gamma}$ = The shear rate.

One may define apparent viscosity by

$$\eta_{ap} = \frac{\tau}{\dot{\gamma}} = \eta_{pl} + \frac{\tau_o}{\dot{\gamma}}. \quad (2)$$

In some cases, where yield stress was not high, it was possible to obtain good values for the intercepts for both rising and falling bob. The mean of these two represents the force necessary to suspend the bob in the liquid. This leads to a determination of the density. In such a case the yield stress can be found without reference to a separate density determination.

A brief narrative description of each experiment will be followed by a summary discussion. All these experiments were performed at 13.8 MPa (2000 psia) of hydrogen.

D-5-5 Solvent-to-Coal Ratio (S/C) = 1.6 (525 K, 486 °F)

Experiment D-5-3, previously reported, yielded very little usable data because of the large quantity of solids formed at 525 K. The viscometer was fitted with a baffle plate in an attempt to improve the quality of the data. The plate was placed horizontally just above the highest position of the bob. It was hoped this would cause the cake of solids atop the bob to be pushed to the side and remixed with the liquid. This expedient was partly successful and the data are shown in Figure 1.

FIGURE 1. VISCOSITY OF SLURRY D-5-5 (S/C = 1.6) AT 525 K (486 °F) AND 13.8 MPa OF HYDROGEN

The data for plastic viscosity were not very reproducible, probably due to fluctuations in the distribution of solids in the liquid phase.

We did not obtain data at $S/C = 1.6$ at higher temperatures. To work at higher temperatures would require a smaller bob.

D-5-6 $S/C = 1.6$ (513 K, 464 °F)

Having previously reported data at 500 K (D-5-1) and in this report at 525 K (D-5-5), we attempted to obtain data at this intermediate temperature. Results are shown in Figure 2. Measurements were difficult. Because of the poor stirring the temperature indicated by the thermocouple was slow to rise. This does not necessarily mean the sample passing by the bob was cold, but it does indicate poor movement of the sample. The points at 12 and 22 minutes seem reliable; the others are based on scattered and insufficient data.

D-5-7 Coarse Grind, $S/C = 1.6$ (450 K, 350 °F)

The reference coal sample used in these measurements has been ground to pass a 200 mesh screen. Since this grind is much finer than would be used in a liquefaction plant, this measurement and one other (G-5-2) were made using a small hand-ground sample of larger particle size. A screen analysis showed

-70 +100	28%
-100 +200	43%
-200	29%.

The transfer of this sample from one autoclave to the other was difficult. A plug formed in one of the lines or valves which interfered with the customary occasional flow of hydrogen through the sample. This plug also prevented draining the sample from the viscometer. The results, shown in Figure 3, are based on data showing in some cases a considerable amount of scatter. The results seem to be essentially reliable, though the turn upward is not sure. Comparison with Figure 7 of the previous Quarterly Report shows that the sample with the finer grind showed greater viscosity.

FIGURE 2. VISCOSITY OF SLURRY D-5-6 (S/C = 1.6) AT 513 K (464 °F) AND 13.8 MPa OF HYDROGEN

FIGURE 3. VISCOSITY OF COARSE COAL SLURRY D-5-7 (S/C = 1.6) AT 450 K (350 °F) AND 13.8 MPa OF HYDROGEN

E-5-1 Fort Lewis Solvent and Coal,
S/C = 1.6 (451 K, 352 °F)

Samples of ground coal and solvent were received from The Pittsburg and Midway Coal Mining Company in June, 1980. The coal was Kentucky Nos. 9 and 14. Our sieve analysis showed

-70 +100	Trace
-100 +140	8%
-140 +200	8%
-200	84%.

Measurements were made with a slurry of this material to find out how much the low temperature thickening might depend on the source of coal and solvent. The results are shown in Figure 4.

The data seem to show clearly the ups and downs depicted for the plastic viscosity although it is not so clear whether the variations were due to changes in plastic viscosity or in yield stress. We have chosen to show this peculiar shape because the data seem to require it. We are not sure that the cause may not have been an instrumental aberration; it seems unlikely that the viscosity would change in this peculiar way.

The yield stress values are very uncertain, not only because of the great scatter in the results but also because the calculation was based on an unknown density. We were unable to obtain any useful data with a descending bob and we have not made an independent measurement of density. We have therefore assumed that the density was the same as for the reference slurries. A subsequent indication (E-5-3) of a higher density for this solvent than for the Wilsonville material leads to the conclusion that the yield stress values shown here are less than the true values by perhaps 0.4 N/m^2 .

F-5-1 S/C = 3.0 (540 K, 512 °F)

In the past we have had the greatest difficulties in the 550 to 600 K range, where viscosities are highest and changes most rapid. We have supposed that by working at greater dilutions we might be able to traverse this region with less difficulty. We might thereafter be able to extrapolate our results to more concentrated slurries. In pursuit

FIGURE 4. VISCOSITY OF FORT LEWIS SLURRY E-5-1 (S/C = 1.6) AT 451 K (352 °F) AND 13.8 MPa OF HYDROGEN

of this goal we made one measurement at a solvent-to-coal ratio of 3.0. The results seemed unsatisfactory, so later measurements were made at a higher concentration of solids.

The results are shown in Figure 5. The curve has been drawn with a peak at about 2 hours because the data seemed to show such a trend. We are reluctant to accept the curve as a true indication of viscous properties.

In the case of this rather thin slurry, it was possible to get some reasonably good data with a descending bob. From the intercepts for both ascending and descending bob operation, we were able to determine the density and these results also are shown in Figure 5. We were surprised to find the declining values of the density, but the data seem to show it clearly.

G-5-1 S/C = 2.6 (540 K, 513 °F)

This measurement was the first of a series at a new solvent-to-coal ratio. It was hoped in this way to be able to measure properties at higher temperatures than would be possible at S/C = 1.6 or S/C = 2.0. The results are shown in Figure 6. The data seemed reasonably satisfactory. It was possible to make a determination of density, and these results are shown also in Figure 6.

E-5-2 Fort Lewis Coal, Reference Solvent,
S/C = 2.6 (540 K, 513 °F)

Since the measurement of slurries made from the coal and solvent from Fort Lewis (E-5-1) showed such high viscosities, a measurement was made using only the coal from Fort Lewis, the solvent being our reference solvent from Wilsonville. Figure 7 shows the results.

The results are difficult to understand. There seemed to be relatively little scatter in the data. Yet the measured viscosities changed in what seemed to be an erratic manner throughout the measurement. The yield stress and density observations seemed to be less variable. The

FIGURE 5. VISCOSITY OF SLURRY F-5-1 (S/C = 3.0) AT 540 K (512 °F) AND 13.8 MPa OF HYDROGEN

FIGURE 6. VISCOSITY OF SLURRY G-5-1 (S/C = 2.6) AT 540 K (513 °F) AND 13.8 MPa OF HYDROGEN

FIGURE 7. VISCOSITY OF FORT LEWIS COAL-WILSONVILLE SOLVENT SLURRY E-5-2 (S/C = 2.6) AT 540 K (513 °F) AND 13.8 MPa OF HYDROGEN

fall in measured density seems very large. One would expect the density to remain nearly constant.

E-5-3 Fort Lewis Coal and Solvent,
S/C = 2.6 (540 K, 513 °F)

These measurements were made with coal and solvent obtained from The Pittsburg and Midway Coal Mining Company. Results are shown in Figure 8. The data seemed satisfactory. It was possible to get only one good determination with the bob descending, so we determined only one value of density at a time of about 30 minutes. This value is 991 kg/m^3 . Comparison with Figures 6 and 7 shows that this density is substantially higher than that of similar slurries with reference coal and solvent, and that the higher density is due to the solvent. The calculated values of τ_0 were based on this one density determination.

G-5-2 Coarse Grind, S/C = 2.6 (540 K, 512 °F)

Transfer of this sample into the viscometer occurred with the same difficulty that accompanied the transfer of D-5-7. A plug formed in the transfer line, interfering with the flow of hydrogen and with the removal of sample by draining. There appeared to be sufficient sample for the measurements, but the data were of poor quality. The data peaks were poorly formed and of low reproducibility. The results are shown in Figure 9. Although the uncertainties are great, comparison with G-5-1 shows that the results, also at this temperature, are dependent on particle size.

G-5-3 S/C = 2.6 (552 K, 534 °F)

The data peaks obtained from this sample were generally well formed and reproducible. The results are shown in Figure 10.

Comparison with a similar run at a lower temperature (G-5-1) shows very little difference. It appears that the expected viscosity peak may begin at a somewhat higher temperature when slurries of greater dilution are examined.

FIGURE 8. VISCOSITY OF FORT LEWIS SLURRY E-5-3 (S/C = 2.6) AT 540 K (513 °F) AT 13.8 MPa OF HYDROGEN

FIGURE 9. VISCOSITY OF COARSE COAL SLURRY G-5-2 (S/C = 2.6) AT 540 K (512 °F) AND 13.8 MPa OF HYDROGEN

FIGURE 10. VISCOSITY OF SLURRY G-5-3 (S/C = 2.6) AT 552 K (534 °F) AND 13.8 MPa OF HYDROGEN

G-5-4 S/C = 2.6 (572 K, 570 °F)

An attempt to make measurements at a higher temperature was not successful. High force was often required to set the bob into motion. The data generally lacked reproducibility. Only a few tentative results could be obtained. After about 20 minutes, a plastic viscosity of about 3.8 mPa·s was estimated, with a yield stress of about 0.9 N/m². After about 2 hours lower values were observed, 1.7 mPa·s and 0.1 N/m². However, these numbers are very uncertain. At the conclusion a large deposit of solids was found on top of the bob. We do not know whether it was there throughout the run or whether it settled out during cooling. It is clear, however, that the variable distribution of these solids causes the random changes in the data. If a quantity of solid material is accumulated on top of the bob, then the measurement will be distorted by the extra weight and also by the removal of these solids from the slurry.

G-5-5 S/C = 2.6 (577 K, 579 °F)

The previous measurement was repeated with the addition of a baffle plate as in Experiment D-5-5. Although these data were also uncertain, especially in the early part of the experiment, some useful results were obtained. They are shown in Figure 11. During the first 5 minutes there appeared to be a rapid thickening, but the data were not sufficient for calculation of the parameters η_{pl} and τ_o .

Preliminary Analysis

A thorough discussion of the significance of these results, together with those previously reported, will appear in the final report. A few comments are appropriate at this time.

Effect of Temperature. A comparison of Experiments D-5-5, D-5-6, D-5-1 (Figure 6 of the Sixth Quarterly Report) and D-5-4 (Figure 7 of that report) shows the effect of temperature from 450 to 525 K for S/C = 1.6. A gradual increase in η_{pl} and τ_o is indicated. Measurements

FIGURE 11. VISCOSITY OF SLURRY G-5-5 (S/C = 2.6) AT 577 K (579 °F) AND 13.8 MPa OF HYDROGEN

at higher temperatures were not successful at this solvent-to-coal ratio. A comparison of $S/C = 2.0$ has been shown previously. For a comparison at $S/C = 2.6$, see G-5-1, G-5-3 and G-5-5. This comparison shows a sharp rise between 552 and 572 K.

Effect of Solvent-to-Coal Ratio. At 540 K a comparison can be made of the effect of concentration from $S/C = 1.6$ to $S/C = 3.0$. Experiment D-5-2 of the Sixth Quarterly Report indicates that at $S/C = 1.6$ (but at a slightly higher temperature) the mixture was too stiff for measurement. Comparison of F-5-1, G-5-1 and B-5-19 (Figure 5 of the Sixth Quarterly Report) shows the expected thinning upon dilution. The effect is dramatic at this temperature. The change with time is also dependent on solvent-to-coal ratio.

Effect of Particle Size. We used a hand-ground sample to assess qualitatively the effect of particle size on the viscous behavior. Two comparisons were made. The first, between D-5-7 and D-5-4 (Figure 7 of the Sixth Quarterly Report), was at $S/C = 1.6$ and $T = 450$ K. The other, between G-5-2 and G-5-1 was at $S/C = 2.6$ and at the higher temperature of 540 K. In both cases the differences were marked, the finer coal showing the higher viscosity. The ratio of plastic viscosities is about 2.7, of yield stress is about 5. A more careful size analysis would be needed to make this comparison quantitative.

Effect of Source of Materials. With the exception of three runs involving coal and solvent from the Fort Lewis, Washington plant, all our measurements were made with a single coal and a single solvent. Comparisons with the Fort Lewis material were made at $S/C = 1.6$ and $T = 450$ K (E-5-1 and D-5-4: Figure 7 of the Sixth Quarterly Report) and at $S/C = 2.6$ and $T = 540$ K (E-5-3 and G-5-1). The plastic viscosity was found to be three or four times as great for the Fort Lewis material in spite of the larger particle size. No good comparison can be made of yield stress because of the lack of density data, but rough indications are that the yield stress was about the same for the two slurries at each S/C ratio. The measurement

E-5-2, although the results were not very satisfactory, seems to indicate that the difference was mainly due to the differences in the solvent.

Density Changes. On several occasions it was found possible to measure density throughout the course of the measurements. In each case the densities were seen to decrease by a few percent. We have not been able to think of any measurement artifact that would explain this change and are therefore disposed to think it is real. It happens that all these results were obtained near 540 K (512 °F). Presumably the reactions involving absorption of solvent and/or dissolution of coal seem to result in some expansion.

Task 5. Calorimetry

A Du Pont Pressure Differential Scanning Calorimeter (DSC) has been used for determinations of specific heat and heat of reaction.

The DSC determines the difference between heat effects in two sample pans. One of the pans is usually empty. The pans sit on a constantan disc which is in good thermal contact with a silver furnace completely surrounding the sample pans. The disc transmits heat to the sample pans. The temperature of this silver furnace is controlled by a chromel-alumel thermocouple and a resistive heater. Although some heat is transferred from the lid and walls of the cell through the atmosphere, the primary means of heat transfer is through the disc. Hydrogen is admitted to the sample chamber through an orifice in the block wall. Temperature difference between the sample and reference platforms is monitored by a chromel-constantan difference thermocouple formed by the junction of the constantan disc with a chromel wire at each platform position. The difference signal between these two thermocouple junctions is amplified and monitored on a recorder. The signal is proportional to the apparent specific heat and the rate of temperature increase.

If energy is released or absorbed in a chemical or physical change the difference signal will display a peak which may be positive or negative.

The area under the peak on a time-base plot is proportional to the energy involved in the transition or other heat effect. The sample platform has an alumel lead wire forming a chromel-alumel thermocouple junction. The sample temperature is monitored by this thermocouple on the temperature recorder after suitable cold junction compensation.

Determination of Energy Change
Involved in Dissolution Reactions

The differential scanning calorimeter was set up to study the heat effects produced by heating coal-solvent mixtures at a constant rate of about 22 °/min from room temperature to 438 °C. The instrument was calibrated for continuous operation, for which the appropriate equation is

$$\frac{dQ}{dT} = m C_p = \frac{KY}{dT/dt} . \quad (3)$$

Here Y is the pen deflection produced by the difference thermocouple and t is time. The calibration covered the range from room temperature to 700 K. The agreement with the previous calibration was not adequate. Two experiments were conducted to obtain calibration based on the heats of fusion of tin and indium, but these did not resolve the difficulty. Since the study of coal-solvent slurries had higher priority, no further attempts were made to find reasons for the disagreement.

A "solvent substitute", a coal-derived material of low vapor pressure at elevated temperature, was used in these experiments. Two experiments were conducted with a mixture of Kentucky No. 9 coal and the solvent substitute at solvent-to-coal ratios of about 1.6. The volatiles evolved during heating may drive off any hydrogen admitted into the sample capsule via a hole in the lid, and prevent solvent-hydrogen reactions. To ascertain if this was happening, a third experiment was performed at solvent-to-coal ratios of 1.6 with the sample placed in an open aluminum pan on the sample platform. The reference platform had a similar pan which was empty. Since heating in an open pan provides more surface area for vaporization as opposed to a sealed capsule, the experimental procedure was slightly

modified to minimize vaporization losses. The solvent was first heated in an open aluminum pan in hydrogen atmosphere from room temperature to 710 K (819 °F) and cooled in situ to room temperature. The coal was mixed with the preheated solvent and the mixture was heated under the same conditions as the samples in the first two experiments.

In each of these three experiments the mixture was heated to the desired temperature, cooled, weighed, and again heated to the same temperature. The deflection obtained during the second run was corrected for sample weight loss and subtracted from the deflections obtained during the first run. The net energy evolved or absorbed per degree change in temperature per unit weight of the starting material was then calculated from Equation (1) where ΔY , the difference between pen deflections during the first and second runs on the sample sample, is written for Y .

Discussion of Results

Figure 12 shows the net energy evolved or absorbed due to reaction between the coal and the solvent. The general shape of the curves appears to be similar for all the experiments, but the agreement between calculated values is not adequate. The following observations are apparent from Figure 12:

- An endothermic effect at 310 to 360 K (97 to 189 °F)
- An exothermic effect at 440 to 500 K (332 to 441 °F)
- Endothermic effect beyond 500 K.

The endothermic effect at lower temperatures may be attributed to starting problems or to loss of water. The exothermic effect may be due to reactions between the coal and the solvent. In all the experiments, a distinct endothermic peak was observed during the second runs at 400 to 500 K. This peak was not so pronounced during the first runs. Interpretation is not self-evident. It may be, as implied by Figure 12, that an exotherm occurring in the same temperature range partly masks the endotherm which appears every time. On the other hand, this endotherm may be some sort of

FIGURE 12. NET ENERGY EVOLVED OR ABSORBED AS A FUNCTION OF TEMPERATURE FOR KENTUCKY NO. 9-SUBSTITUTE SOLVENT SLURRY IN HYDROGEN ATMOSPHERE (5.67 to 6.65 MPa)

melting phenomenon which occurs more prominently in the product from the first run than it does in the coal-solvent mixture. In that case the apparent exotherm of Figure 12 would represent an artifact of data treatment, not a real phenomenon.

The endothermic effect beyond 500 K appears to be the result of further vaporization of volatile matter. It appears that the disagreement in the calculated values of the net energy is due to uncertainty in the baseline. In fact, the deviation from zero at the higher temperatures may all be due to baseline shift.

Determination of Energy Change for Mixtures with Other Coals

The following coals were mixed with preheated solvent at a solvent-to-coal ratio of 1.6 and heated in hydrogen atmosphere at a constant rate of about 22 °/min from room temperature to 663 K (734 °F).

- (1) Kentucky Nos. 9 and 14 supplied by Pittsburg and Midway
- (2) Ohio coal from Pittsburgh No. 8 seam
- (3) Illinois No. 6 coal from Christian County.

The samples were encapsulated in aluminum pans. A small hole was made with a #80 drill and the hole partially plugged by a chromel wire of smaller diameter. This procedure was adopted to provide minimum surface area for vaporization of volatile components.

Discussion of Results

Figures 13 through 15 show the net energy evolved or absorbed for these mixtures. In case of the Kentucky Nos. 9 and 14 coal plus preheated solvent mixture (Figure 13), it is evident that the general shape of the curves from the two experiments is similar. Baseline shift appears to have caused displacement of the two curves. Except for the mixture with Illinois No. 6 coal, the observations in all other cases are similar to Kentucky No. 9 plus solvent mixture (Figure 12). In the case of the mixture with Ohio coal (Figure 13), the apparent exothermic effect appears to cover a wider range of temperature. This may not be significant because a shift

FIGURE 13. NET ENERGY EVOLVED OR ABSORBED AS A FUNCTION OF TEMPERATURE FOR KENTUCKY NOS. 9 AND 14 AND PREHEATED SOLVENT SLURRY IN HYDROGEN ATMOSPHERE (5.67 to 6.65 MPa)

FIGURE 14. NET ENERGY EVOLVED OR ABSORBED AS A FUNCTION OF TEMPERATURE FOR OHIO COAL-PREHEATED SOLVENT SLURRY IN HYDROGEN ATMOSPHERE (5.67 to 6.65 MPa)

FIGURE 15. NET ENERGY EVOLVED OR ABSORBED AS A FUNCTION OF TEMPERATURE FOR ILLINOIS NO. 6 COAL-PREHEATED SUBSTITUTE SOLVENT SLURRY IN HYDROGEN ATMOSPHERE (5.27 to 6.65 MPa)

in the baseline could displace the curve one way or the other. It is not clear why the mixture with Illinois No. 6 coal (Figure 15) did not show the effect at 500 K.

Specific Heat of Coal-Solvent Mixtures

The specific heats of the coal-solvent mixtures were determined directly from the pen deflection and the rate of temperature rise. The appropriate equation for calculating specific heat from continuous heating operation is

$$C_p = \frac{K (Y_2 - Y')}{m \, dT/dt} , \quad (4)$$

where

C_p = Specific heat of the mixture, J/gk

K = Cell calibration constant, J/mv min

Y_2 = Pen deflection during the second run after correcting for sample weight loss, mv

Y' = Pen deflection with empty pans on both platforms, mv

m = Sample mass at the beginning of the first run, gm

dT/dt = Heating rate, (K/min).

Equation (4) gives the specific heat with poor accuracy due to uncertainty in the baseline. Figures 16 through 18 show calculated specific heats for the several coal-solvent mixtures. The general scatter in the specific heat data in all cases is probably due to the uncertainty in the baseline. This uncertainty is avoided in the method described in the Sixth Quarterly Report of this series.

Discussion

The results of our attempts to obtain useful quantitative data on coal-solvent slurries by DSC have proved disappointing. The ever present baseline problems make it difficult to obtain quantitative data by a continuous heating method. Heats of reaction in the case of sharply defined

FIGURE 16. SPECIFIC HEAT AS A FUNCTION OF TEMPERATURE FOR KENTUCKY NO. 9 COAL-SUBSTITUTE SOLVENT SLURRY IN HYDROGEN ATMOSPHERE (5.27 to 6.65 MPa)

FIGURE 17. SPECIFIC HEAT AS A FUNCTION OF TEMPERATURE FOR KENTUCKY NOS. 9 AND 14 COAL-PREHEATED SUBSTITUTE SOLVENT SLURRY IN HYDROGEN ATMOSPHERE (5.27 to 6.65 MPa)

FIGURE 18. SPECIFIC HEAT AS A FUNCTION OF TEMPERATURE FOR OHIO COAL-PREHEATED SUBSTITUTE SOLVENT SLURRY IN HYDROGEN ATMOSPHERE (5.27 to 6.65 MPa)

peaks or specific heat by intermittent heating are procedures which can give good results because these procedures circumvent the problems of baseline shift.

There are, however, some more fundamental problems. The problems of high vapor pressure and of good contact with hydrogen both require that the sample capsule be capable of being pressurized. The combination -- i.e., obtaining good hydrogen contact in the presence of a volatile sample -- would probably represent an insoluble problem even with a pressurized sample capsule. Furthermore, were it possible to obtain quantitative heat of reaction data one would still have to establish the stoichiometry of the corresponding chemical change. This would require a degree of accuracy in analysis unobtainable with such small samples. We conclude that satisfactory thermal data will require a calorimeter designed to operate with much larger samples.

Plans for Next Quarter

A small amount of analytical work remains to be completed on samples from viscosity measurements. No other experimental work, with the possible exception of a few enthalpy determinations, remains to be done. The final report will be prepared.