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THERMOPHYSICAL PROPERTIES OF COAL LIQUIDS

Final Report

By
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April 23, 1982

Work Performed Under Contract No. AC22-79ET14941

Battelle Columbus Laboratories
Columbus, Ohio

U. S. DEPARTMENT OF ENERGY

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FINAL REPORT

on

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ABSTRACT

Thermophysical properties for coal-solvent slurries were determined in the range 300-600 K, in some cases extending to 700 K. Density, viscosity, thermal conductivity, and enthalpy were determined. A recycle solvent from the Wilsonville SRC-I plant and a KY-9 coal were used. Rheology was studied with a reciprocating cylinder viscometer designed to operate at elevated pressure and temperature. Viscous properties were found to follow the Bingham plastic model. A high-viscosity peak in the range 500-600 K was characterized by very high values of yield stress. At other temperatures the slurries were nearly Newtonian. Time and temperature dependence of viscous behavior were studied. Densities were determined by high temperature pyknometer, thermal conductivities by the transient line-source technique, and enthalpies by drop calorimeter and by pressure DSC.

SUMMARY

Introduction

The design engineer needs to know the properties of the material that is to pass through his plant. In particular, the heat-transfer characteristics of coal-solvent slurries will greatly influence the design of the preheating facility. This program was initiated in order to make thermophysical property data available to the designer of an SRC I demonstration plant. The results, however, are applicable in a general way to preheater design in any direct coal liquefaction process.

Ideally heat would be transferred by convective mixing through a preheater pipe. If the thermophysical properties were known, the heat transfer rates could be found through modeling. The viscosity of the slurries may be high, especially as caking coals pass through the temperature range of plasticity. Under such conditions, turbulence may not be achievable and heat transfer may be by conduction alone and may be very poor. Overheating may result in caking, which may plug the pipe.

One way of investigating these phenomena is to study the changes in thermophysical properties as the slurry is heated through the temperature range of the preheater. The problem is made difficult by the elevated pressure of the preheater, made necessary to prevent vaporization of the solvent, swelling of the coal and coke formation. Therefore, experiments need to be conducted under hydrogen pressures typically of 13.8 MPa (2000 psi).

In this work, KY No. 9 coal and a recycle solvent from the Wilsonville SRC-I pilot plant were used. The coal was more finely ground than would be typical of a liquefaction plant. Much of the work was done at greater dilution than would be typical. Results showed that both these variables had substantial effect on the viscosity. Since the conditions in the preheater were not reproduced exactly in these experiments, the results cannot be transferred directly to the preheater without exercising considerable discretion.

Rheology

Viscosity of coal-solvent slurries was measured in a concentric-cylinder device in which the inner cylinder moved up and down axially, pumping the sample back and forth through the annular space between the cylinders. Shear stress was determined from the force applied to the inner cylinder. Shear rate was determined by measuring the rate of motion of the inner cylinder. Apparent viscosity is the ratio of shear stress to shear rate. For a Newtonian liquid it does not depend on shear rate.

Coal-solvent slurries at low temperatures were found to be nearly Newtonian in behavior. In the high-viscosity "gel" region the departures from Newtonian behavior became very great. These materials were found to behave very much like Bingham plastics; that is, the shear stress varied linearly with shear rate as in Newtonian liquids, but the intercept at zero shear rate (the yield stress) was not zero. Thus, a considerable, sometimes very great force could be applied to the static system before the inner cylinder began to move. At higher temperatures, the coal became soluble and the system returned nearly to Newtonian behavior and low viscosity. When cooled, this liquid showed higher viscosities than the original slurry except that it did not pass again through the high-viscosity gel condition.

Viscosities were measured at constant temperature by charging the cold slurry into a preheated viscometer. At temperatures below about 500 K (440°F) for slurries with solvent-to-coal ratio of 1.6, or at higher temperatures for more dilute slurries, a thickening effect in the first few minutes was followed by a slow thinning. At about 500 K for $S/C = 1.6$, or at about 550 K (530°F) for $S/C = 2.0$, a more profound thickening took place leading to high plastic viscosities and very high yield stresses. Static yield stresses appeared to be much higher than the dynamic yield stresses determined by extrapolation from data on the moving cylinder. For this reason, it became impossible to operate the viscometer in the region of greatest thickening.

The high-viscosity peak was found to depend greatly on concentration. For more concentrated slurries the rise in viscosity was much greater and began at a lower temperature than for more dilute slurries. The effect was also much greater for finely ground coal than for a coarser grind. A few

experiments showed that the source of coal and solvent also influenced the viscosity.

These results point to a complex behavior of coal slurries in the preheater pipe. At the temperature of thickening there will be a buildup of thick material on the wall while the cooler and thinner slurry passes through the center, insulated from the hot wall. As the temperature increases, the central part will thicken also. Now heat transfer will be by conduction alone. Further on, the wall will become hot enough for the coal to become soluble and for the viscosity to drop. Material at the wall will then act as a lubricant for plug flow. Subsequently the higher temperatures will reach the core and the whole mass will become fluid and turbulent again.

Thermal Conductivity

The transient line-source technique was used for these measurements. A thin vertical platinum wire was used both as heater and thermometer. When a current is passed through such a wire, sufficient to raise its temperature a few degrees, the temperature-time curve for about one second can be analyzed to yield the thermal conductivity of the liquid. The liquid must be completely at rest and the data must be obtained before thermal convection sets in. Data were obtained throughout the temperature range of interest. Operation was especially satisfactory in the high-viscosity gel region, where convection could not occur. This is just the region in which the data are most needed. For all materials, solvent, slurry and product liquid, thermal conductivity was found to decrease slowly as the temperature rose. Results for these several samples did not differ greatly, all falling within the range 0.16 to 0.08 W/m K.

Calorimetry

A differential scanning calorimeter (DSC) capable of operating at pressures up to 1000 psi of hydrogen was used for studies of specific heat and heat of reaction.

The method proved inadequate for heat-of-reaction measurements. Vaporization of sample and failure of access to the hydrogen atmosphere were

the two greatest problems. By substituting a high-boiling solvent it was possible to obtain a few essentially negative results. No considerable heat effect was detected for the solution reaction between solvent and coal. The hydrogenation reactions take place rapidly only at temperatures beyond those reached in the measurements. Therefore, the absence of any exotherm corresponding to hydrogenation is not considered to be a significant finding. A flow calorimeter has been suggested as the best alternative for obtaining these data.

Specific heat data were obtained by DSC, using a high-boiling substitute solvent and by a more reliable drop calorimeter, using the reference coal and solvent. The data were similar. The enthalpy of solvent, coal slurry and product liquid were found to differ slightly.

Density

The densities of a few samples were measured with a pyknometer consisting of a small pressure vessel and valve. The data were satisfactory up to the temperature at which gas was evolved, even at elevated pressure. Densities were found to decrease with increasing temperature in a nearly linear manner.

Conclusions

Methods have been developed which give valuable results for all the properties to be measured except heat of reaction, for which an alternative method has been suggested. The results have been useful in the design of an SRC-I plant. Further work is required to provide heat-of-reaction data, to correct theoretical inadequacies in the viscosity measurements, to develop a method for the plastic region, and especially to broaden the results to materials of representative origin.

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I. INTRODUCTION

In the autumn of 1979 a program was initiated to study thermophysical properties of coal-solvent slurries under conditions similar to those existing in the preheater section of coal liquefaction plants. The results were expected to be applicable in a general way to all direct liquefaction processes. However, the program was designed specifically to support the design of an SRC-I demonstration plant intended to be built in Kentucky. Therefore, a KY No. 9 coal and a solvent simulating a recycle solvent from this plant were specified as the reference coal and solvent. Almost all measurements were made with these materials and with a simulated product liquid prepared from these materials. A statement of objectives and scope is presented here.

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 were prepared by a short residence time technique. These samples, together with the starting materials, were subjected to careful analysis. Most of the experiments were conducted with mixtures of solvent and pulverized coal. The residues from these experiments were characterized by solvent extraction techniques.

Task 3. Rheology. A falling-cylinder viscometer has been used to characterize the slurries. With this instrument it is possible to determine the shear stress as a function of shear rate. Most of the measurements were made at constant temperature.

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

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

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

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

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

During the first month of the program an experimental plan was developed. The effect of the plan was to focus attention on the coal and solvent intended for the SRC-I plant, to emphasize the rheology studies as of the greatest and most immediate importance, and to emphasize the need for developing methods of measurement which could subsequently be used to study other combinations of materials. The plan is reproduced in Appendix A.

At the conclusion of the program it is clear that these major objectives have been met, although not all the measurements planned have been accomplished. Two areas of work remain incomplete. The first has to do with the variety of materials that could not be included. There was indication in some of the viscosity measurements that the source of the coal and solvent--especially the solvent--could have a very great effect on the results. The viscosity peak appears to occur not at all for non-caking coals. Therefore all the measurements, but especially the rheological studies, need to be extended to other materials. The effect of concentration and particle size needs to be studied further as well.

The second major item of unfinished research is the determination of the heat of reaction between coal and solvent and between the slurry and hydrogen. The calorimetry with DSC showed only that heat effects below 650 K are small and that DSC, as used here, is not adequate for the measurement. A method involving high-temperature flow calorimetry has been proposed.

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II. MATERIALS

Although the proposed program called for measurements on a diverse group of coals and solvents, the initial planning phase, accomplished in consultation with PETC and HPCI, developed an emphasis on one "reference" coal and solvent. As the program evolved, almost all the measurements were made with the reference materials. All measurements reported here were made with these materials unless stated otherwise. The reference coal and solvent were chosen to match, as closely as possible, the materials to be used in the proposed SRC-1 Demonstration Plant. They were obtained with the aid of Air Products and Chemicals, Inc.

The OBJECTIVE of this task was to provide uniform well-characterized materials for the several measurements to be made and to characterize the samples after measurement as to the extent of conversion into product soluble in tetrahydrofuran.

COAL

The reference coal used in this program was KY #9 coal, mined at Ken #4 Mine of the Peabody Coal Company, Beaver Dam, Ohio County, KY in December 1979 or January 1980. It was crushed to -3 in. and washed but not dried. The coal was received in our laboratory in March 1980 where it was reduced by hand to about -2 in. and air dried. The coal was then carefully divided into equivalent portions and stored in glass jars under argon. The coal was withdrawn from storage as needed and ground under protective atmosphere to -200 mesh. A small hammer mill in a nitrogen-filled glove box was used. Material retained on a 200-mesh screen was returned to the mill. The ground sample was kept in a protective atmosphere until used.

Since the coal was ground in relatively small quantities in order that storage of the powder be kept to periods of a few weeks, the grinding procedure was not uniform and the particle-size distribution probably varied considerably throughout the work. As an example of the size distribution, a

single sample was examined with a Coulter Counter. The results are shown in Figure II-1.

Analysis of the coal gave the results shown in Table II-1.

SOLVENT

The reference solvent used in this program was taken from a single 5-gallon container of Wilsonville Recycle Solvent designated CPDU 115 and received in November 1979. An analysis is shown in Table II-2.

A fractional distillation was carried out. The temperatures were converted to the corresponding boiling points at atmospheric pressure. The results are shown in Figure II-2 as a continuous line.

A method has been developed using gas chromatograph (GC) to produce simulated distillation curves. The method is similar to ASTM 2887-73. A standard series of n-paraffins of known boiling points is injected into a GC column for which retention time is proportional to boiling point. A series of retention times corresponding to known boiling points is obtained which can be used to characterize other volatile samples.

The Wilsonville Recycle Solvent (CPDU 115) used in these studies was analyzed in duplicate by this GC technique and the results are compared in Figure II-2 to the boiling point curve by distillation. Data obtained by APCI using a similar GC method for the same solvent are also shown. The Battelle GC simulation and distillation curves agree well above about 285 C. The APCI results are a little better at lower temperatures. Differences may be due to changes in GC response factors as boiling point changes.

PRODUCT LIQUID

In several cases, properties of the slurry were to be compared with properties of the product obtained by heating the slurry to liquefaction temperatures. To provide samples of this simulated product liquid two preparations were made by a short residence-time technique.

FIGURE II-1. SIZE DISTRIBUTION BY COULTER COUNTER

TABLE II-1. ANALYSIS OF KY #9 REFERENCE COAL

	As Rec'd	Dry Basis
<u>Proximate Analysis, wt %</u>		
Moisture	4.82	--
Ash	7.87	8.27
Volatile matter	38.74	40.70
Fixed carbon	<u>48.57</u>	<u>51.03</u>
	100.00	100.00
<u>Ultimate Analysis, wt %</u>		
Moisture	4.82	--
Ash	7.87	8.08
Carbon	70.40	73.96
Hydrogen	4.98	5.23
Nitrogen	1.18	1.24
Chlorine	0.04	0.04
Sulfur	3.03	3.18
Oxygen (by difference)	<u>7.68</u>	<u>8.08</u>
	100.00	100.00
<u>Sulfur Forms, wt %</u>		
Pyritic	1.18	1.24
Sulfate	0.06	0.06
Organic	<u>1.79</u>	<u>1.88</u>
	3.03	3.18
Heating Value (HHV), MJ/kg	29.53	31.02
Btu/lb	12,697	13,340

TABLE II-2. ANALYSIS OF CPDU - 115 SOLVENT

Carbon	87.9%
Hydrogen	8.2%
Oxygen	2.8%
Nitrogen	1.0%
Sulfur	0.5%
Oils (pentane soluble)	97.7%
Asphaltenes (benzene soluble)	1.9%
Preasphaltenes (pyridine soluble)	0.4%

FIGURE II-2. COMPARISON OF DISTILLATION CURVES FOR WILSONVILLE DECYCLE SOLVENT (CPDI 115)

FIGURE II-3. COAL LIQUEFACTION APPARATUS

AC2 is Equipped with an Internal Heater

AC3 is Equipped with an Internal Cooling Coil

A quantity of the reference coal was ground to -100 mesh with liquid nitrogen cooling but exposed to air. This was used for the preparation of a simulated preheated sample. A 2:1 solvent-to-coal slurry was preheated in an autoclave to 470 K (386°F). The charge was transferred with nitrogen pressure to a second autoclave which had been preheated to 757 K (921°F). The system was pressurized with hydrogen to about 10 MPa (1500 psi). The sample temperature rose in 8 minutes to 732 K (848°F) and was controlled there for 2 minutes. We estimate that this temperature pattern results in the same conversion as would be achieved by holding the sample at exactly 732 K for 4.8 minutes.

The charge was then transferred to a third autoclave where it was cooled rapidly to 360 K (188°F), then transferred to a glass bottle. The product was kept under argon and refrigerated. Analysis by solvent extraction led to the results shown in Table II-3. This material was given the designation 4/80.

In the second preparation the coal and solvent (S/C = 1.6) were preheated to 466 K (379°F) and transferred to the second autoclave which was preheated to 750 K (890°F). The system was pressurized with 912 MPa hydrogen and the sample temperature rose to 724 K (843°F) in 4.5 minutes and was held above this temperature for 4 minutes. The average temperature during the reaction period was 730 K (854°F). The reaction mixture was then quenched to 363 K (197°F) by transfer to a third autoclave. The product of this reaction was also stored in glass, under nitrogen, in a refrigerator. This product was called 9/80.

Samples of the unfiltered reaction products were extracted with pyridine, toluene and hexane to determine concentration of unreacted coal, preasphaltenes, asphaltenes and oils. The ratio of solvent to coal in the products was also determined by measuring the ash content of the pyridine insolubles. A comparison of the two products is given in Table II-3. The values in the table refer to the complete product, including solvent.

It had been intended that the second liquid, designated 9/80, should represent a solvent-to-coal ratio of 1.6. Because of inadequate mixing in the first autoclave, however, the transfer of coal to the reaction autoclave was incomplete so that the product represents a solvent-to-coal ratio of 2.2.

TABLE II-3. ANALYSIS OF PREPARED PRODUCT LIQUIDS

Product Designation	4/80	9/80
Pyridine Insoluble	7.3%	5.6%
Preasphaltenes	7.0%	15.5%
Asphaltenes	7.6%	8.7%
Oils	78.0%	70.2%
Solvent-to-Coal in Products	2.56%	2.18%

This is the material used in subsequent experiments calling for a product liquid.

III. RHEOLOGY

An understanding of the rheology of coal-solvent slurries as they are heated to reaction temperature is of the greatest importance to the engineer designing a liquefaction plant. For caking coals the apparent viscosity passes through a maximum. In this "gel" stage the material is resistant to flow in the tubular preheater. Turbulence cannot be achieved and the heat transfer is slow. Since the phenomenon is time and temperature dependent, the task of modeling the flow is very difficult.

The OBJECTIVE of this task was to determine the rheological characteristics of coal-solvent slurries as they depend on time, temperature, concentration, and source of materials.

Only one coal-solvent pair was studied in detail and the measurements were incomplete in the region of highest viscosity. Nevertheless a great deal was learned about the behavior of these materials, and the groundwork was laid for productive work in the future.

PREVIOUS WORK

Most of the work on rheology of coal-oil slurries and of coal-derived liquids has been done at atmospheric pressure and therefore not far above room temperature. Viscosities of concentrated slurries were found to be non-Newtonian and to be generally higher than predicted for spherical particles¹. Coal-oil suspensions made with brown coal have been found to increase in viscosity with aging, even at room temperature². The viscosity of coal-derived liquids has been related to asphaltene and preasphaltene content^{3,4}. Aging of coal-derived liquids, especially in the presence of oxidizing gases, has been found to increase viscosity⁵.

A few attempts have been made to measure viscosity at elevated temperature and pressure. Pilot-plant experience has shown that coal-solvent slurries sometimes pass through a high-viscosity stage while in the preheater.

In a continuing program at Oak Ridge National Laboratory a continuous coal-liquids flow system has been instrumented for measurement of viscosity and density⁶. The slurry is pumped through a length of heated tubing after which it passes through a constant-temperature section equipped with pressure taps. By varying the flow rate it is possible to vary shear stress and shear rate and thus to study the rheology of non-Newtonian mixtures. Since the residence time in the heated tubing is short, the viscosity of newly made sample can be determined. A pronounced viscosity peak at about 640 K has been observed with IL No. 6 and KY No. 9 coals and Wilsonville recycle solvent. Recently measurements of viscosity, and surface tension and density as well, have been reported by workers at Brigham Young University.⁽⁷⁾ The measurements were made with product liquids only, not with slurries. Viscosity was measured by the rolling-ball method, suitable only for Newtonian liquids.

THE VISCOMETER

A reciprocating concentric-cylinder viscometer was developed at Battelle for measuring the viscous properties of Synthoil liquids at elevated temperature and pressure⁸. It seemed well suited for the slurry measurements. The mechanical system is simple. There is little loss due to friction. The reciprocating action of the inner cylinder, the "bob", tends to keep the slurry mixed. Data can be obtained quickly. The bob can be operated over a wide range of shear rates.

The apparatus is shown in Figure III-1. It depends on the axial movement of concentric cylinders resulting in a pumping action which forces liquid to flow in the direction opposite to that of the inner cylinder in the space between the cylinders. A mixing autoclave, shown on the right, holds the sample at a controlled temperature prior to transfer into the viscometer.

A 0.3L autoclave constitutes the outer cylinder of the viscometer. A cylindrical bob (9) has a radius approximately 1 mm less than the inside radius of autoclave. The bob is attached by tubing through a connector (6) to a large Alnico V bar magnet (5) and, by means of a thin rod, to a second smaller bar magnet (3). The magnets move freely inside tubing extending from the top of the autoclave. The bob is hollow, the space inside communicating

FIGURE III-1. VISCOMETER AND MIXING AUTOCLAVE

with the autoclave atmosphere through the suspension tube. Outside the pressure system are located two large coils (4). When a current is passed through these two coils in opposite directions, an upward or downward force is exerted on the bob, depending on the direction of current flow. A second pair of coils (2) surrounds the smaller magnet. Motion of this magnet induces a current in these coils whereby the direction and rate of motion of the bob are detected. A vibrator helps to keep the bob moving smoothly.

Good temperature control is important. Because of the high heat capacity of the system it is important that the heaters be closely coupled to the metal of the autoclave. A sheathed heater is welded to the body of the viscometer. It provides the primary temperature control. A control thermocouple is inserted into the bottom of the autoclave where it makes good contact with the metal. A 3-action proportional controller is used. Two band heaters are used, one around the flange, the other around the cover, independently controlled to keep these parts at the same temperature as the body of the autoclave. A copper enclosure around the valves below the autoclave (10) is provided with strip heaters to keep the valves and tubing at the same temperature. The principal heat leak is through the water-cooled tube extending out the top of the autoclave. Its cooling effect is well compensated by the band heaters. A sheathed thermocouple (8), immersed in the sample just above the bob, shows the sample temperature. A similar temperature-control system keeps the preheater autoclave at constant temperature.

Valves and 1/4-inch tubing are provided, as shown, by which sample can be transferred from one autoclave to the other. Ports for the introduction and withdrawal of gas, for pressure measurement and control and for a safety valve are provided, several of which are shown (1,7). A sensitive backpressure regulator controls the pressure. The mixing autoclave is stirred with a magnetically driven (13) turbine-type agitator (11). The viscometer autoclave is stirred only by the action of the bob. As an aid in keeping the solids in suspension, a burst of gas is occasionally admitted from below.

Calibration

The viscosity of a fluid in the apparatus can be calculated from the velocity and force acting on the bob. The equations have been worked out for Newtonian liquids^{8,9}. Although this procedure for determining shear stress and shear rate in non-Newtonian systems is not rigorous, we have used it as a suitable approximation.

Driving Coils

The force applied to the bob was derived by calibration from the current passed through the lifting coils. The same current passes, in opposite sense, through both coils so that they act together to raise or lower the bob. It would be ideal if the force applied to the bob were constant throughout its travel. Figure III-2 shows that the force is nearly constant over a span of about 1 cm. Here the apparent weight of the bob assembly in grams is shown as a function of the position of the bob relative to its resting place at the bottom of the autoclave. Two curves are shown, at two settings of the power supply. A decade resistor is used to control the power supply, and the setting of this resistor is shown. The current through the coils is about 0.2 mA per Ω .

In the two cases shown in Figure III-2 the force is directed upward, so that the lifting force is greatest near the center of the stroke. The actual weight is arbitrary, since in use the buoyancy of the bob is significant. From a series of such curves it has been found that, near the position of maximum force, the force is proportional to the current in the coils and therefore to the control setting in ohms.

Sensing Coils

In order to sense the rate of movement of the bob a second magnet and pair of coils has been used. This magnet, also cylindrical, is much smaller than the drive magnet. It is supported in a smaller tube above the heavier magnet. A pair of coils only a few windings thick has been wound around this

FIGURE III-2. LIFTING FORCE AT TWO SETTINGS OF THE POWER SUPPLY

tube in such a way that the signals induced by the movement of the two poles are in the same direction. The sum is recorded on a strip chart. The magnitude of the signal is proportional to the rate of movement of the bob and is virtually independent of the position of the bob. A simple integrating circuit gives indication of the position of the bob, although this information is not needed in the measurement. It is a simple matter to determine the relationship between the chart reading in mV and the rate of movement of the bob.

These calibrations make it possible to know the force applied to the bob and the rate of movement of the bob. To convert this information into shear stress applied to the liquid and the resulting shear rate is more difficult. It is possible to make calculations based on the assumption of Newtonian behavior of the liquid. For this purpose the following equations may be used. For the shear stress,

$$\sigma = \frac{F}{2\pi h R_b} \frac{(\beta^2 - 1)}{(\beta^2 + 1)} \quad (\text{III-1})$$

and for the shear rate,

$$\dot{\gamma} = \frac{v_b}{R_b} \left[\frac{(\beta^2 + 1)}{(\beta^2 - 1)} \ln \beta - 1 \right]^{-1} \quad (\text{III-2})$$

where

h is the height of the bob

R_b is the radius of the bob

R_c is the radius of the cylinder

$\beta = R_c/R_b$

F is the force applied to the bob

v_b is the rate of movement of the bob.

For Newtonian liquids, $\eta = \sigma/\dot{\gamma}$. Because end effects are neglected and because of the difficulty in making sufficiently accurate measurements of R_b and R_c it is preferable to calibrate by using standard liquids.

Calibration with Known Liquids

The force applied to the coils has been converted to units of shear stress by application of Equation III-1. The relationship between bob velocity and shear rate has been established by reference to standard liquids. For higher viscosities ($> 1 \text{ mPa}\cdot\text{s}$), standard calibrating oils have been used*. At low viscosities we have calibrated with toluene and checked the results with water and methanol.

Figure III-3 shows a sample of the data, obtained with water at 337 K ($\eta = 0.44 \text{ mPa}\cdot\text{s}$). The power setting (in Ω) is shown for each excursion of the bob. Traces to the left indicate a rising bob, to the right a falling bob. Peaks read from the traces are plotted in Figure III-4. Points to the right of zero represent a rising bob, and to the left, a falling bob. Frictional effects are particularly troublesome at low viscosities. This is probably the reason for the scatter in the data and for the failure of the two lines to meet at zero velocity. Results have been based on the slopes of the lines for the rising bob. In this case the slope is $11.5 \text{ } \Omega/\text{mV}$. The calibration constant, k , is defined as the ratio of viscosity ($\text{mPa}\cdot\text{s}$ or cP) to the slope of the line (Ω/mV) for the rising bob. For this case $k = 3.8 \times 10^{-2}$. The zero on the vertical scale is arbitrary, since the upward force includes bob buoyancy which depends on the density of the liquid.

PROCEDURE

In some cases, when the properties of the sample were thought to be relatively stable, the sample was loaded into the viscometer autoclave and subsequently heated to the temperature of measurement. The rise and fall of the bob were observed as a function of the force applied. These data were plotted on linear paper. An example for a slowly changing sample is shown in Figure III-5, except that in this case the data are expressed in units of

*Cannon Instrument Company, State College, PA.

FIGURE III-3. SAMPLE DATA, WATER AT 337 K

FIGURE III-4. DATA FOR WATER AT 337 K, PLOTTED IN THE FORM SHEAR STRESS VERSUS SHEAR RATE

shear stress and shear rate. The zero on this shear-stress scale was not easily established, since some force was required to keep the bob just suspended in the liquid. This force was related to the mass of the bob assembly and to the density of the liquid. For some liquids the force required to balance the bob could be determined, thereby leading to a determination of density. For liquids displaying a high yield stress this balance point could not be determined experimentally because of the great force required to set the suspended bob into motion in either direction. For these liquids the zero point on the shear-stress scale was found by calculation based on density determined in a separate experiment. Shear rate was related to bob velocity through calibration with a Newtonian standard.

In Figure III-5 a force equivalent to about 3.6 on the shear-stress axis was required to overcome gravity. Two sets of points are shown, one for a rising, one for a falling bob. The gap between the two intercepts at zero shear rate is a measure of the yield stress. It will be seen that the data follow the Bingham-plastic model. The viscous behavior is characterized by two constants, as follows:

$$\tau = \tau_0 + \eta_{pl} \dot{\gamma} \quad (\text{III-3})$$

where τ_0 is the dynamic yield stress and η_{pl} is the "plastic viscosity", that is, the slope of the line of Figure III-5. The self-centering behavior of the bob works better on the rising stroke, therefore results were based mostly on the upper line.

In the case of slurry samples, which were expected to change with time, the slurry sample was loaded into the auxiliary autoclave and stirred while the viscometer was heated to the selected measurement temperature. The pressure was raised to 13.8 MPa (2000 psi) by pressurizing both autoclaves with hydrogen. The sample was transferred by adjusting the pressures slightly and opening connecting valves. The temperature of the sample rose to within a few degrees of the control temperature in the first minutes and to a stable temperature (± 1 K) in about 5 minutes.

The data were reduced by plotting a family of curves, each curve showing the change in velocity of the bob with time for a constant current in the lifting coils. Figure III-6 shows an example of such a family of curves,

FIGURE III-5. SAMPLE OF VISCOSITY DATA

Solvent/Coal Ratio: 3.0
Temperature: 570 K (566°F)

FIGURE III-6. SAMPLE DATA FOR SAMPLE B-5-19 (S/C = 2.0) AT 539 K (511 °F)

only three of which are shown. The initial drop in bob velocity (peak height in mV) represents a thickening effect. This is followed (5 to 20 minutes) by a thinning and a subsequent second thickening.

Because of the nature of the slurries, especially in their high-viscosity state, the data were poorly reproducible. These plots served to smooth the data. Cross plots were then made, showing the change of bob velocity with coil current. These plots, similar to Figure III-5, gave slopes and intercepts from which η_{pl} and τ_0 were found by application of calibration constants.

RESULTS

In general the behavior of coal-solvent slurries and product liquids appeared to follow the Bingham plastic model. There were deviations from straight lines, often due to scatter in the data, but perhaps indicating that the actual behavior of these materials lies somewhere between the Bingham plastic and the pseudo-plastic models. The data gave a decidedly better fit to a straight-line than to a power-law curve. Therefore results are reported in terms of the parameters η_{pl} and τ_0 of Equation III-3.

The results of the determinations of viscous properties of slurries as a function of time, each at constant temperature, are shown in Appendix B. Several examples, together with some generalizations, are shown in this section.

Figure III-7 shows results for two slurries at a relatively low temperature. The experiment was continued for a long time. Initial changes, especially for the more concentrated slurry, were rather large and rapid. The very great effect of solvent-to-coal ratio is evident. At this modest temperature, especially in the case of the more dilute system, departures from Newtonian behavior were not great.

By way of contrast, Figure III-8 shows results at a higher temperature. During the course of a quarter hour the material passed through the high-viscosity gel region. At a solvent-to-coal ratio of 2.0 this slurry was considerably more dilute than the 1.6 slurry planned for plant use. Yet the plastic viscosity showed a rapid rise followed by a marked decrease while the

FIGURE III-7. VISCOUS PROPERTIES OF SLURRIES
AT 13.8 MPa H₂

FIGURE III-8. VISCOSITY OF COAL-SOLVENT SLURRY
AT 596 K (612°F)

yield stress rose to unknown but very high levels. The values shown for τ_0 are dynamic yield stresses. That is, they are found by extrapolation of observations on a moving bob. The static yield stress, that is, the stress required to put the bob into motion from a position of rest, was observed to be much greater. During the interval in which no data were obtained it was found to be impossible to move the bob, although the force available was very much larger than that used to obtain the data shown. It was because of these very high values of static yield stress that it was not found possible to study the more concentrated slurries throughout the gel region. Even when the bob motion could be started in this plastic region, it was with such large force that the resulting shear rates were beyond the linear shear stress vs shear rate region.

Effect of Temperature and Time

As temperature rises viscosity usually decreases. This pattern was followed for the liquids in this study except for a time-dependent thickening that occurred in the case of the coal-solvent slurries. Figure III-9 shows an example of slurry data along with results for viscosity determinations on the reference solvent and on the product liquid 9/80. All these measurements were made at 13.8 MPa of hydrogen pressure. In the case of the solvent and the product liquid, no change with time occurred. For the solvent, the yield stress was found to be negligibly small. For the product liquid, values of τ_0 approximately equal to 0.03 N/m^2 were measured. These are near the lower measurement limit.

In the case of the slurry measurements shown in Figure III-9, values reached 15 min after mixing were chosen for illustration. In most cases the changes were not rapid after this elapsed time. The peak at about 300°C would have been noted at a higher temperature at shorter times, as will be shown later. The magnitude of the thickening effect depends largely on the high values of the yield stress. These will also be shown in later plots.

FIGURE III-9. COMPARISON OF TEMPERATURE VARIATION OF PLASTIC VISCOSITY FOR COAL LIQUIDS

Low-Temperature Thickening

The coal slurries undergo changes with time, even at the lower measurement temperatures. With reference to Appendix B, Figures B-1 and B-14 (see also B-22) show that at 450 K a thickening effect in the first 15 min is followed by a gradual decline in both plastic viscosity and yield stress. While both parameters seem to be involved in the initial thickening, the subsequent thinning is primarily due to a decrease in plastic viscosity. The effect is accelerated at 500 K.

High-Temperature Thickening

In order to make the data plots B-1 through B-13 more accessible for comparative purposes, the results have been summarized in Figures III-10 and III-11. The high-temperature gel formation, the major feature of the rheological behavior of these slurries, is clearly visible. The effect is first noted as a general heightening of the plastic viscosity level at 531 K. At 539 K a continuing increase in plastic viscosity is noted. The change in yield stress becomes evident at 556 K. At 566 K the first indications of a subsequent thinning can be seen, but the material returns to a really low viscosity only at 587 K. All these effects appear after the passage of time of half an hour or more. The short-time formation and dissolution of the gel-like product occurs at higher temperatures.

At its maximum the high apparent viscosity owes more to the high yield stress than to the plastic viscosity. It appears, however, that the yield stress begins to decline before the plastic viscosity has reached its peak. Perhaps this is an indication of a transition from a semi-solid with high yield stress to a short-lived highly organized liquid with high viscosity to, finally, a simpler liquid of low viscosity.

In order to plot the rheological constants as a function of temperature, the time dimension must somehow be removed as a variable. One way to do this is to plot the plastic viscosity and yield stress at fixed values of time. This has been done in Figures III-12 through III-15. These plots do not correspond to any real heating schedule. One could, alternatively, select

FIGURE III-10. PLASTIC VISCOSITY OF SLURRY WITH SOLVENT-TO-COAL RATIO OF 2.0

FIGURE III-11. YIELD STRESS OF SLURRY WITH SOLVENT-TO-COAL RATIO OF 2.0

FIGURE III-12. RHEOLOGICAL CONSTANTS OF COAL SLURRIES AT 5 MINUTES

FIGURE III-13. RHEOLOGICAL CONSTANTS OF COAL SLURRIES AT 10 MINUTES

FIGURE III-14. RHEOLOGICAL CONSTANTS OF COAL SLURRIES AT 15 MINUTES

FIGURE III-15. RHEOLOGICAL CONSTANTS OF COAL SLURRIES
AT 25 MINUTES

a temperature-time curve and cross-plot at appropriate times. The results still would not relate exactly to slurries heated according to that heating curve. Nevertheless, Figure III-12 approximates a rapid heat-up and III-15 a slower heat-up of the respective slurries.

With reference to the $S/C = 2.0$ slurry, for which data are most extensive, one notes, at short times, a greater dip in plastic viscosity near 550 K followed by a sharper peak near 590 K than in the curves for slower heating, where the peak is broader. Furthermore, the yield stress rises sharply with temperature for fast heat-up while for slower heating the yield stress is less significant.

Concentration of the Slurry

A desirable outcome of this research would be the ability to predict the viscous properties of a concentrated slurry ($S/C = 1.6$) at short holding times. Both plastic viscosity and yield stress reach very high values for concentrated slurries. It was not found possible to make measurements at $S/C = 1.6$ beyond 530 K. It may have been possible to extend the measurement range a little with a smaller bob, designed to shed high-solids slurries. The basic problem is that these materials do not flow. The bob tends to lift a quantity of sample rather than to pump it back and forth. In the peak region the sample becomes a paste and cannot be handled with the apparatus available. A pipe-line viscometer can overcome this problem but it has other problems instead.

For this reason measurements have been made at several concentrations in order that extrapolation could be resorted to in order to get results for concentrated slurries. Figures III-12 to III-15 show how great is the effect of solvent-to-coal ratio. Not only do the rheological constants vary enormously as the concentration is changed, but the temperatures at which changes take place are greatly affected. At $S/C = 1.6$ the material was too thick for measurement at 530 K while at $S/C = 2.6$ it is not altogether clear whether the viscosity peak occurs at all. It is concluded that extrapolation along a S/C axis would at best be uncertain and would require a lot of closely-spaced experiments.

Particle Size

One might expect the effect of particle size on the time-temperature behavior of coal slurries to be considerable. The effect is likely to be related to surface area, whether caused by surface effects, absorption and swelling, or dissolution. Figures III-16 and III-17 show comparisons of two experiments using a hand-ground coarse coal with experiments under the same conditions, but using the standard grind. The data are shown in Appendix B in Figures B-14, B-18, B-22, and B-23 together with descriptions of the experiments. Only the smooth curves are reproduced here. The coarse grind was 29 percent -200 mesh; the fine grind was 100 percent -200 mesh (see Chapter II and Appendix B). The magnitude of the effect may be surprising, especially as it is shown in the yield stress. The comparisons were made on the low-temperature side of the viscosity hump. At higher temperatures and longer times the larger particles would probably make their contribution toward thickening.

The only control of particle size in these experiments was the assurance that all the samples passed through a 200-mesh screen. In the case of the "coarse" grind the control was considerably less, since this material was simply ground by hand. For precise results the particle size would need to be controlled much more carefully.

The coal used for these measurements was ground to -200 mesh in order that large particles would not interfere with the movement of the bob. The necessity for this was demonstrated by the difficulties experienced with the coarse grind. The fine particles remained in suspension much more easily than would the larger particles of a coarser grind. But the grind intended for plant use was much coarser than that used in these measurements. The use of such a coarser grind and the resulting data more directly applicable to plant design would have required a much larger instrument and would have given more serious stirring problems.

Other Materials

During the course of the work it was found desirable to compare results with those obtained at the Fort Lewis pilot plant. Measurements were

FIGURE III-16. VISCOSITY AT 450 K (350°F) AND S/C = 1.6 OF SLURRIES D-5-4 (FINE) AND D-5-7 (COARSE)

FIGURE III-17. VISCOSITY AT 540 K (512°F) AND S/C = 2.6 OF SLURRIES G-5-1 (FINE) AND G-5-2 (COARSE)

therefore made on three samples composed of coal received from Fort Lewis, two of these samples containing solvent also obtained from Fort Lewis. The samples and results are described in Appendix B. For some reason the behavior of the viscometer appeared to be somewhat erratic and results were not of the highest quality. It is clear that plastic viscosities were much higher than with the reference materials, even though the grind was not so fine. The last experiment, B-26, of Appendix B seems to point to the Fort Lewis solvent as the cause of the higher viscosities.

In a preliminary experiment, a non-caking coal was used in measurements extending nearly to 700 K. No indication of a viscosity peak was observed at a solvent-to-coal ratio of 2.0.

It is clear that the phenomenon of a viscosity maximum with high yield stress is strongly dependent on the source of materials. It is therefore important that studies of the phenomenon be made using the coal and solvent intended for plant use.

Density Data

During several of the measurements (see Figures B-18, -19, -21, and -26) it was found possible to measure density by observing the force necessary to suspend the bob in the liquid. The volume of the bob was found from similar measurements in a liquid of known density. These results were in agreement with those obtained by pycnometer. The curious feature was the change with time. These results are discussed in Section VI.

DISCUSSION

Validity of the Results

The procedures developed here seem to give a close approximation to the true picture concerning the rheological behavior of coal-solvent slurries during heat-up. The behavior has been shown to follow approximately the Bingham-plastic relationship. Calibration with Newtonian liquids of known viscosity has given us confidence in the numbers reported for plastic viscosity, at least in samples not departing greatly from Newtonian behavior.

On the other hand, the determinations were not based on rigorous theory. The assumption was made that the shear-rate calibration, based on Newtonian liquids, is applicable also for Bingham plastics. At best this assumption is only an approximation. A better theory of bob operation needs to be applied to these results, either to validate or to correct them.

The concern over the inadequacies of the data-reduction procedures for highly non-Newtonian samples is considerably diminished because of the even greater difficulties in bob operation for these materials. When yield stress was high the material tended not to flow like a liquid but to separate into a thinner fraction which was pumped past the bob and a thicker fraction which was carried up and down atop the bob and was probably also collected at the bottom of the autoclave. In many cases the bob behavior gave erratic readings. The excessive scatter is sometimes obvious in the plotted results in Appendix B. The provision of a baffle plate above the bob was of some help, and a more closely fitted plate would give further improvement. However, the nature of the sample in the region of the viscosity peak imposes a limitation on any apparatus with an intermittent application of shear.

An even more significant limitation on the validity of the results in the gel region derives from the very great dependence of viscous properties on particle size, on source of coal, on concentration, and especially on time and temperature. Both in the laboratory and in the plant, there are likely to be such variations in these parameters as to make it virtually impossible to assign precise numbers to the rheological "constants".

Because of the difficulties in specifying, determining, or holding constant these many parameters of material and apparatus, the instrumental difficulties in these measurements seem less significant. Although in some cases the uncertainty in the results may have reached 20 or 30 percent, the pattern of behavior is clearly shown. The reliability of the results was much greater in the near-Newtonian regions where most of the difficulties discussed here were absent.

The "Gel" Region

Throughout much of the time-temperature space the slurries behave in near-Newtonian fashion. Even the more concentrated slurries do not depart

greatly from ideal behavior. However, the interaction between coal and solvent causes dramatic changes within the viscosity hump.

Plastic viscosities measured in the viscous region were seldom above 20 mPa·s. These are not high viscosities, and should cause no difficulties in flow. Values of dynamic yield stress, however, have exceeded 10 N/m². Behavior of the bob indicated that static yield stresses were much higher. The material becomes paste-like. Shear rates at the walls are very high. Plug flow is the result. When flow stops, as at the end of the stroke of the bob, the material tends to set up so that high forces are required to initiate movement again. Therefore the difficulties in flow are much greater than would be supposed on the basis of plastic or apparent viscosities.

Effect of Pressure

The effect of pressure on viscous properties was not directly studied in this work. Previous experience, together with occasional observation, showed that viscosity is increased slightly by increase in pressure. The effect is small enough to be essentially negligible in the context of the present study. Elevated pressure is required, of course, to prevent loss of solvent. Hydrogen was chosen as a pressurizing gas to prevent any possible changes due to oxidation. The effect of pressure on the rate of the processes leading to changes in viscosity was not studied. Thus the temperature range in which the viscosity peak occurs may be somewhat pressure-dependent.

The Need for Further Measurements

With the exception of the high-viscosity peak, the viscometer described here has proved to be adequate. It is capable of measuring very high viscosities if the yield stresses are low. Adjustments in bob size would improve low-viscosity accuracy. Temperature and pressure capabilities are adequate. The measurements were less than adequate in the gel region.

The material to be dealt with in this region is not a liquid, but a paste. It does not flow; it has to be pushed. Therefore we believe that a capillary flow viscometer would be preferable. A continuous-flow instrument

has some attractive features but is not well suited to a study of the effect of time, which has been shown to be crucial in an understanding of the phenomenon.

We believe that a suitable instrument could be devised on the basis of a two-autoclave arrangement similar to that shown in Figure III-1. A third autoclave would be required to hold and mix the cold slurry prior to the start of the experiment. Each of the two vessels in the viscometer would be fitted with a piston by the operation of which the sample would be forced back and forth through a connecting capillary tube. These pistons would be driven by the application of hydrogen pressure. Therefore no mechanical drive would be required and the pistons would not have to fit tightly. Motion of the pistons would be detected as in the present viscometer. Force would be determined by measuring the pressure difference. Shear rate would be varied by varying the pressure. Since the entire sample would age at the same rate, the effect of time would be easily determined. The tube could be large enough for measurements with a coarser coal grind. The method could, perhaps, be used at low viscosities by substituting a smaller tube, but probably less effectively than the reciprocating cylinder method.

IV. THERMAL CONDUCTIVITY

For liquids in laminar flow through tubes the rate of heat transfer depends on the thermal conductivity. In order to model the heat exchanger and so be able to design it for maximum efficiency, it is necessary to know this property. The way in which thermal conductivity changes with increasing temperature in coal-solvent slurries is important in itself, even if absolute values are uncertain.

Therefore, the OBJECTIVE of this task was to make measurements of thermal conductivity in representative coal-solvent slurries including the dependence on temperature and solvent-to-coal ratio. The most significant subtask was deemed to be the design and construction of an instrument capable of these measurements.

A number of researchers have reported the successful application of transient techniques to the measurement of thermal conductivity in liquid media. Van Der Held and Van Drunen⁽¹⁰⁾ used the line source or heated wire technique to measure the thermal conductivity of water and strong acids. For these measurements, natural convection in the liquids was not significant because the measurements were made before convection currents could be established. Recently, McLaughlin and Pittman⁽¹¹⁾ have reported a comprehensive study of the application of the line source technique to the determination of the thermal conductivity of toluene from 250 to 400 K. They claim an accuracy of 1 percent, based on a comparison with existing data and on a thorough analysis of various possible sources of error.

These studies show that transient techniques such as the line source can be effectively applied to measure thermal conductivity of liquids. In some cases, the transient technique can be designed to eliminate many of the problems associated with steady state techniques. These problems are replaced with a new set of difficulties such as the requirement to acquire transient temperature and heat flux data, and more complex data reduction techniques. However, the recent availability of accurate digital data acquisition equipment which is coupled with a micro-computer makes the line source technique a very powerful method for thermal conductivity measurements.

THERMAL CONDUCTIVITY MEASUREMENT TECHNIQUE

The method applied to the experimental determination of thermal conductivity of the coal slurry is the transient line source method. The line source method has been selected for the present application because it offers the following benefits:

- Small sample volume for measurement
- Fast response, minimizing settling and coking problems
- A relatively simple design compared with steady state techniques
- An accurate, proven technique.

The line source probe has been demonstrated to be an effective technique for the measurement of thermal conductivity of fluids.^(10,11) Reported accuracies for a carefully designed experiment are 1 percent. Although some compromises were required in the present experiment, due to the elevated temperature and pressure test conditions, a 5 or 6 percent accuracy level was achieved.

Line Source Method

The temperature response of an infinitely long line heat source immersed in an infinite medium has been determined by Jaeger.^(12,13) The analysis indicates that the line source temperature rise can be described by the following logarithmic approximation when $\alpha t/r^2 \gg 1$:

$$T - T_o = \frac{Q/\ell}{4\pi k} \ln \frac{4\alpha t}{1.781 r^2} \quad (\text{IV-1})$$

where α is the thermal diffusivity of the medium, t is the time, r is the probe radius, Q/ℓ is the heat input per unit length, and k is the thermal conductivity of the medium. For a constant heat input, the temperature rise of the line source describes a straight line when plotted versus the logarithm of time. The slope of the curve is given as

$$\frac{dT}{d \ln t} = \frac{Q/\ell}{4\pi k} \quad (\text{IV-2})$$

and is inversely proportional to the thermal conductivity of the medium. The slope is independent of all other properties of the fluid. Rewriting this expression, we have

$$k = \frac{Q/\ell}{4\pi} \left(\frac{dT}{d \ln t} \right)^{-1} \quad (IV-3)$$

The logarithmic approximation is valid only when $\alpha t/r^2 \gg 1$. An estimate of the measurement error is given in Table VI-1 for a range of values of $\alpha t/r^2$. The time, t , in this expression refers to the initial time or the time of the first temperature measurement. The test is assumed to extend at least 10 times the initial time.

TABLE IV-1. MEASUREMENT ERROR IN LINE SOURCE
DETERMINATION OF THERMAL CONDUCTIVITY

$\frac{\alpha t}{r^2}$	Measurement Error, %
50	< 1
20	2
10	5
5	11

In addition to the nondimensional parameter $\alpha t/r^2$, the logarithmic approximation represented by Equation (IV-1) depends on the density-specific heat product of the line source element relative to the material being measured. The error estimate given in Table IV-1 assumes the density-specific heat product of the line source element is approximately equal to that for the semi-infinite medium in which the element is immersed. This error estimate will be approximately correct if the ratio of the density-specific heat product between the element and the medium is greater than 0.5 and less than 2.0. Outside this range, refer to Reference (11) for a correction factor.

Wire Temperature Determination

The change in temperature of the wire in Equation (IV-3), dT , can be related to the measured change in resistance of the wire,

$$\frac{dT}{T_o} = \frac{dR}{R_o} \left(\frac{dR/R_o}{dT/T_o} \right)^{-1}, \quad (\text{IV-4})$$

where

$$\frac{dR/R_o}{dT/T_o} = aT_o, \quad (\text{IV-5})$$

and a is the temperature coefficient of resistance. The product aT_o is approximately 1 for platinum and tungsten, but it can vary by 25 to 30 percent due to differences in the metallurgical properties of the wire. A careful calibration of the specific wire resistance element is required in order to obtain accurate thermal conductivity measurements.

The change in resistance of the wire can be expressed in terms of the change in voltage divided by the current:

$$\frac{dR}{R_o} = \frac{dV}{IR_o}. \quad (\text{IV-6})$$

The heat input to the wire is

$$Q = I^2 R_o. \quad (\text{IV-7})$$

Combining these terms, the measured conductivity becomes:

$$k = \frac{aR_o^2 I^3}{4\pi\ell} \left(\frac{dV}{d \ln t} \right)^{-1}. \quad (\text{IV-8})$$

In the development of Equation (IV-8) it was assumed that the heat input to the wire is constant. It was further assumed in Equation (IV-6) that the current is constant. These assumptions are theoretically incompatible if the wire resistance changes due to electrical heating. However, if the change

in wire resistance is held to less than 1 or 2 percent, the change in power and/or current will be negligible during a test. This constraint on resistance change is consistent with the need to keep the temperature change of the wire to a minimum during a test to minimize radiation and convection effects, and to minimize the uncertainty of the actual measurement temperature.

From Equation (IV-8) it is clear that there are five parameters to be measured in the determination of thermal conductivity using the heated wire technique. The length of the wire, the wire resistance, the wire current, and the voltage across the wire as a function of time, all can normally be measured to 1 percent accuracy or better. The final parameter, the temperature coefficient of resistance, α , is a basic property of the wire material which must be determined through additional measurements.

Determination of Temperature Coefficient of Resistance

A search of available literature has resulted in room temperature values of the parameter " α " for platinum wire which vary by 30 percent. Little data are available at higher temperatures. Furthermore, results obtained by Battelle indicate that " α " may depend on the specific metallurgical or physical characteristics of the wire or the wire surface. Measurements of resistivity of platinum wire as a function of temperature on two separately purchased samples of 0.025 mm dia. platinum wire are presented in Figure IV-1. A least squares fit straight line has been determined for each of the wire lots for the data above 400 K. The value of " α " determined from the slope of each data set differed by nearly 7 percent at a given temperature. It is therefore recommended that for measurements of thermal conductivity requiring the highest level of accuracy, a great deal of care be given to the determination of " α ".

The following empirical relationships have been developed to correlate the value of " α " obtained in the present tests for a platinum wire:

FIGURE IV-1. MEASUREMENTS OF PLATINUM RESISTIVITY VS. TEMPERATURE

Lots #1 and #2	$a = \frac{4.25}{T^{1.25}}$	$300 \leq T \leq 400 \text{ K}$
Lot #1	$a = \frac{0.95}{T}$	$400 \leq T \leq 600 \text{ K}$
Lot #2	$a = \frac{1.02}{T}$	$400 \leq T \leq 600 \text{ K}$

In these expressions, T is the initial wire temperature in degrees Kelvin. The wires were all 0.025 mm diameter and 70 to 80 mm in length. The measurements were made while the wires were immersed in the coal/solvent mixture.

The data scatter about the correlation expression is approximately ± 3 percent below 400 K and ± 2 percent above 400 K.

Experimental Approach

Line Source Gage Design

Design constraints have been imposed on the line source gage by the experimental requirements. The tests were conducted in an autoclave because of the temperature and pressure ranges required of the measurements. Thus, the length of the wire element and the size of the terminals were limited by the geometry of the autoclave. It is desirable to make the wire long in order to reduce end effects and convection effects. The wire length was limited to 80 mm by the physical dimensions of the autoclave.

The coal slurry required vigorous stirring during the heating cycle. The wire was therefore partially enclosed in tubing in order to protect the wire from breakage. A sketch of the gage design is presented in Figure IV-2. A photograph of the autoclave head with the line source gage attached is presented in Figure IV-3. Figure IV-4 is a closeup of the gage. A stainless steel hemi-cylinder provides a shield for the wire while allowing for exposure to the fluid in the autoclave. This tube also provides support for the electrical leads.

The wire element is silver soldered to flexible brass terminals such that the wire is in a slight amount of tension. A small amount of movement of

FIGURE IV-2. DETAILED SKETCH OF LINE SOURCE GAGE

FIGURE IV-3. LINE SOURCE GAGE ATTACHED TO
AUTOCLAVE HEAD

FIGURE IV-4. LINE SOURCE GAGE CLOSE-UP

the terminals due to differential thermal expansion of the stainless steel tubing relative to the wire can be absorbed in the brass terminals.

Data Acquisition

The measurement of the initial wire resistance and the current through the wire during a test can be accomplished to a high degree of accuracy. The measurement of resistance change, or voltage change, of the wire during the test is much more difficult and requires special attention to achieve accurate results.

The change in voltage drop across the heated wire due to a 1 percent increase in (absolute) temperature is approximately 1 percent. The initial voltage applied to the wire is typically 1.5 volts. During the few-second heating pulse, the wire voltage changes by about 15 millivolts. It is difficult to accurately resolve a 15-millivolt voltage change in a 1.5 volt-signal.

In order to remove the 1.5-volt baseline signal so that the small voltage change can be accurately measured, the line source wire element was placed into a Wheatstone bridge. A schematic of the circuit, along with the data acquisition system, is shown in Figure IV-5. The fixed resistors and the bridge balancing resistor are power resistors which do not change when voltage is applied to the bridge. The bridge imbalance voltage during a heating pulse can therefore be used to determine the change in voltage drop across the wire:

$$\Delta V_{\text{wire}} = \frac{R_1 + R_2}{R_2} \Delta V_{\text{bridge}} \quad (\text{IV-9})$$

where R_1 is the wire resistance and R_2 is the value of the fixed resistors in the bridge (250 Ω in Figure IV-5).

The bridge voltage is monitored using a Norland 2001A Waveform and Data Analysis Oscilloscope.* The Norland records data in digital form and contains a micro-computer with which the data can be subsequently analyzed.

*Norland Corporation, Fort Atkinson, Wisconsin.

FIGURE IV-5. LINE SOURCE PROBE TEMPERATURE MEASURING CIRCUIT

Using the Norland, the line source data can be analyzed immediately following a test so that the quality of the test can be ascertained and the measured conductivity determined within minutes of the test. The Norland system includes a CRT monitor display, a flexible disk memory, a printer, and a plotter.

Verification of Technique

Thermal Conductivity Measurements in Toluene

The thermal conductivity measurements in toluene have been obtained in order to validate the proposed experimental procedure. Toluene has been selected for this validation because of the work done by McLaughlin and Pittman.⁽¹¹⁾ They have reported thermal conductivity measurements in toluene from 250 K to 400 K, and have recommended toluene as a standard for thermal conductivity measurements.

The temperature response of the line source gage to a constant heat input is presented in Figure IV-6. The initial resistance of the gage was 16.3Ω at room temperature. The energy input to the gage was 7.8 milliwatts/cm. The minimum resolution of the Norland is approximately 0.7 millivolts which corresponds to 0.015 K for the conditions of this test. Combined with the random circuit noise level, a noise level of approximately 0.05 K, or 1.5 percent of the signal, is generated as indicated in Figure IV-6. This noise occurs at a high frequency and can be significantly reduced by filtering the signal.

A plot of the wire temperature change versus the logarithm of time is presented in Figure IV-7. The plot covers a time range of from 0.25 seconds to approximately 1.5 seconds. The slope of this curve has been computed by evaluating the least-squares-fit straight line for the 200 data points between 0.25 seconds and 1.25 seconds. This process has the effect of averaging the data scatter of this signal and results in an accurate slope in spite of the random noise level of the measurement.

The resultant thermal conductivity is presented in Figure IV-8 along with additional results using both platinum and tungsten wire elements. The

FIGURE IV-6. TEMPERATURE RESPONSE OF PLATINUM WIRE ELEMENT

FIGURE IV-7. TEMPERATURE CHANGE VERSUS LOGARITHM OF TIME

FIGURE IV-8. TOLUENE THERMAL CONDUCTIVITY DATA

measured values of thermal conductivity using the platinum wire compare remarkably well with the results of McLaughlin and Pittman. The data are within 1 percent of published values over the entire temperature range.

The results obtained using the tungsten wire compare with the other results; however, they exhibit a somewhat larger degree of scatter. The maximum deviation from the published results is approximately 3 percent. The greater degree of uncertainty of the tungsten wire data compared with the platinum wire data is likely due to an uncertainty in the temperature coefficient of resistance. Also, the voltage output of the line source gage for the tungsten wire is only 1/2 the output using platinum. Thus, the random measurement error is larger relative to the signal level.

RESULTS

Experimental Procedure

The thermal conductivity measurements were carried out in a 46-mm diameter autoclave pressurized to 13.8 MPa. The tests on a given mixture began at room temperature with the mixture added to the autoclave and pressurized. Between tests, the mixture was continuously stirred in order to maintain an even distribution of particles.

The line source technique requires a constant and uniform temperature throughout the test medium during the measurement. Thus, the temperature of the autoclave was maintained at a constant temperature, to within 0.5 K, for 15 to 20 minutes before each test. Before each measurement, the stirrer was turned off and the autoclave temperature was monitored for several minutes as the convection currents decreased. A test was conducted after the convection currents were zero and the temperature stability was acceptable.

For each mixture, several measurements were obtained at room temperature. The mixture was then heated while stirring to a new temperature, generally 30 to 50 K higher, and the experimental procedure was repeated. For a given coal/liquid mixture, a measurement series from room temperature to the highest temperature was conducted in a continuous process over a period of 8

or 10 hours. Each measurement point required 30 to 40 minutes, thus only 12 to 15 temperature points could be obtained per mixture per day. In most cases, several testing days, using fresh coal/liquid mixture samples each day, were required to generate sufficient data to cover the required temperature range with a statistically significant sample of data.

To measure the thermal conductivity, the response of the line source probe to resistance heating was recorded by the Norland. The signal was analyzed to determine if convection was present. If the signal appeared to be valid, the thermal conductivity was calculated. The line source signal was then stored for later analysis.

It had been anticipated that experimental problems would increase as the slurries entered the "gel" region. In fact, this region gave the least trouble, since the very high viscosities prevented convective circulation and therefore extended the period of time during which Equation (IV-8) was found to hold.

Thermal Conductivity Measurements

The results of the thermal conductivity measurements are presented in Figures IV-9, IV-10, and IV-11 for three solvent-to-coal ratios:

- 3:1 solvent-to-coal ratio
- 2:1 solvent-to-coal ratio
- 1.6:1 solvent-to-coal ratio.

All measurements were at 13.8 MPa (2000 psi) of hydrogen. In each case, the results indicate a gradual decrease from the room temperature value of thermal conductivity as the temperature increases. The measurements drop more rapidly in the temperature range of the gel formation until about 650 K. Beyond this point, the measurements in the 3:1 mixture and the 1.6:1 mixture remain constant to the maximum temperatures reached, about 700 K. There appears to be no difference in the thermal conductivity between these two mixtures at 650 K and above. At 700 K and above, a significant amount of solids formation occurred in the mix and no useful data could be obtained.

A tabulation of the data presented in Figures IV 9, IV-10, and IV-11 is presented in Appendix C.

FIGURE IV-9. MEASURED THERMAL CONDUCTIVITY OF A 3:1 SOLVENT-TO-COAL MIXTURE AT 13.8 MPa H₂

FIGURE IV-10. MEASURED THERMAL CONDUCTIVITY OF A 2:1 SOLVENT-TO-COAL MIXTURE AT 13.8 MPa H₂

FIGURE IV-11. MEASURED THERMAL CONDUCTIVITY OF A 1.6:1 SOLVENT-TO-COAL MIXTURE AT 13.8 MPa H_2

The thermal conductivity of the product liquid for a 2.2:1 solvent-to-coal mixture is shown in Figure IV-12. The trend for this fluid is similar to the previous results. Overall, the thermal conductivity of the product liquid at temperatures below 500 K is 10 to 15 percent less than the mixture. Above 600 K, the product liquid thermal conductivity agrees with the mixture results.

Figure IV-13 presents the measured thermal conductivity for the coal solvent used in the liquid/coal mixtures. These data indicate a nearly linear drop in conductivity from room temperature up to 700 K. The measured thermal conductivity of the solvent is 16 to 18 percent less than the coal mixtures at 700 K.

Although a certain amount of experimental data scatter is evident in the results presented in Figure IV-9 through IV-13, the accuracy of the measurements is believed to be very near the ± 5 percent figure estimated at the beginning of this project. With the exception of the two highest temperature points in Figure IV-10, the maximum data scatter is ± 6 percent. If there are no significant systematic errors due to the experimental procedure, we would expect the true thermal conductivity to be within ± 6 percent of the mean of these data.

Comparison of Measurements with a Theoretical Thermal Conductivity Model

The line source probe has been demonstrated to provide accurate thermal conductivity measurements in homogeneous, isothermal fluids. The application of this technique to the measurement of the bulk thermal conductivity of a multiphase medium could be questionable if the relative scale of the inhomogeneities are larger than the real measurement volume. In order to support the line source probe experimental measurements and to provide guidance to the correlation of the conductivity data, an investigation of available analytical models of thermal conductivity has been conducted.

In a heterogeneous mixture, liquid-liquid or solid-liquid, the important properties of the components which will determine the mixture thermal conductivity are the volume fraction, the particle size distribution

FIGURE IV-12. MEASURED THERMAL CONDUCTIVITY OF THE PRODUCT LIQUID,
2.2:1 LIQUID-TO-COAL MIXTURE AT 13.8 MPa H₂

FIGURE IV-13. MEASURED THERMAL CONDUCTIVITY OF THE COAL SOLVENT
AT 13.8 MPa H₂

in the case of a solid, and the thermal conductivities of the component materials which could be temperature dependent. For coal liquid, the solubility of coal in the solvent is also an important parameter.

A theoretical model for thermal conductivity of a heterogeneous mixture has been proposed for mixtures with a high concentration of particles.⁽¹⁴⁾ The thermal conductivity of the mixture is:

$$k_m = k_s \frac{2 + (AB - 1)x}{2 + (A - 1)x} \frac{2(1 - x) + ABx}{2(1 - x) + Ax} \quad (\text{IV-10})$$

where

$$A = \frac{3}{B + 2}$$

$$B = \frac{k_c}{k_s}$$

and k_m is the mixture conductivity, k_s is the solvent conductivity, k_c is the coal conductivity, and x is the volume fraction of the coal in the liquid.

In order to apply this expression to the liquid/coal mixture, it was necessary to specify the thermal conductivity of the coal particles. Since this information was not available, the value for the coal thermal conductivity was chosen to make Equation (IV-10) agree with the data for the 1.6:1 liquid-to-coal data. Equation (IV-10) was then used to predict the thermal conductivity of the other two mixtures.

The thermal conductivity of the coal was chosen to be 0.19 W/mK. The average value of the data presented in Figure IV-13 was used as the thermal conductivity of the solvent.

The results of the predicted thermal conductivity for all three mixtures is compared with the data in Figure IV-14. The three straight lines represent the predicted thermal conductivity for the three mixtures. The upper line is for the 1.6:1 mixture, the middle line is for the 2:1 mixture, and the lower line is for the 3:1 mixture. The changing level of the thermal conductivity prediction is due to the difference in solid particle loading in the three mixtures. Although the 3:1 mixture data appear to be slightly higher than the estimate, the data generally agree with the estimate up to

FIGURE IV-14. COMPARISON OF THERMAL CONDUCTIVITY MEASUREMENTS WITH EMPIRICAL RELATIONSHIP

approximately 400 K. At higher temperatures, the coal begins to react with the solvent and the theoretical estimate would not be expected to agree with the data. Up to 600 K, however, the data retain the same order as below 400 K; the 1.6:1 mixture is highest and the 3:1 mixture is lowest.

Summary of Results

Thermal conductivity measurements have been made in coal/solvent mixtures to 700 K using the transient line source technique. Through the use of digital data acquisition instrumentation which can monitor, store, and analyze the transient response of the line source probe, the transient technique is found to be both accurate and convenient to use. In this report, the line source probe theory is reviewed, and the important design parameters are discussed for selecting the line source element size, input power level, and measurement time.

Thermal conductivity data are presented for three mixtures:

- 1.6:1 Liquid-to-coal ratio
- 2:1 Liquid-to-coal ratio
- 3:1 Liquid-to-coal ratio.

In each case, data were obtained as the mixtures were heated from room temperature through the swelling temperature or gel phase, at a pressure of 13.8 MPa (2000 psi). Data are also presented for the coal solvent and the product liquid resulting from a 2.2:1 liquid to coal mixture.

The results indicate a decrease in thermal conductivity as the temperature increases. For the coal-solvent slurries, the thermal conductivity shows a drop in value at about the temperature of dissolution. At higher temperatures there is little further change in thermal conductivity. Although there are differences in the room temperature conductivity due to the different levels of coal loading in the mixtures, the measurements indicate that all mixtures seek approximately the same value above 650 K.

V. CALORIMETRY

The heat of reaction between coal and solvent and the heat of hydrogenation involving gaseous hydrogen are unknowns in the liquefaction process. These quantities have much to do with plant design since they determine how much heat needs to be added or taken away. Preheater design also requires a knowledge of specific heat as well as the heats of any reactions taking place during the preheating stage.

The first OBJECTIVE of this task was to explore the use of differential scanning calorimetry (DSC) as a tool for determining the heat effects accompanying liquefaction. To the extent possible by this method, these heats were to be determined. A further objective was to determine specific heats, either by DSC or by the more conventional method of mixtures.

With respect to the reaction with hydrogen, producing an exotherm, the problem of (mutually exclusive) access to hydrogen and containment of solvent was partially solved by using a special high-boiling solvent. However, no heat effect was detected. With respect to the dissolution reaction between coal and solvent, the heat effect should have appeared in our thermograms, but it was not detected. With respect to specific-heat measurements, some results were obtained, but they are less reliable than results of drop calorimetry.

Thus the results of our DSC work were either negative or insufficiently reliable. Therefore a complete description of this work is relegated to Appendix D and only a brief summary is presented here. The drop calorimetry is described in more detail.

DIFFERENTIAL SCANNING CALORIMETRY

Measurements were made in sealed capsules, but with a pressure-equalizing hole, in a hydrogen-pressurized DSC cell obtained from du Pont.

The Calorimeter

At the heart of the DSC is a constantan disk shaped to include two raised pan positions. A chromel wire is attached at the center of each pan position. The electrical signal between these wires is a measure of the difference in temperatures between the two pan positions. An alumel wire at the sample-pan position allows for a temperature measurement. Sample pans, which may contain sample or reference material, are placed on the pan positions. Heat transfer from pan to constantan disk brings the pan contents to near the temperature of the thermoelectric junctions.

The constantan disk is supported by a silver furnace which surrounds the disk and sample pans. The furnace may be heated at a rate controlled by a thermocouple in good thermal contact with the furnace. Because of the high thermal conductivity of silver, the temperature of the furnace is uniform. The difference between the amount of heat transferred from the two pans is proportional to the signal displayed by the difference thermocouple. The instrument may be calibrated to show the specific heat of a sample undergoing continuous or intermittent heating or the heat effect accompanying melting or some other phenomenon.

Measurements

Measurements were made by intermittent and by continuous heating, in an attempt to obtain reliable specific heat values and at least some qualitative results related to the heat of dissolution and reaction with hydrogen.

The Problem of Volatility

The most difficult special problem in this work was related to the volatility at high temperature of the coal and especially the solvent. To prevent volatilization of the sample a sealable capsule was required. Yet the sealed capsule prevented access of hydrogen. Further, the capsules available would hold no more than three atmospheres of pressure at most. Pen excursions accompanied changes in pressure, so that it was not possible to balance the

internal sample pressure with increasing calorimeter pressure. Therefore the temperature range for our reference solvent was severely limited.

A "substitute solvent" was obtained from Air Products and Chemicals. It was derived from coal and had low volatility at elevated temperatures. By sealing the sample in the capsule but providing a very small hole, it was possible to heat to 700 K with very little loss in sample weight. One experiment was conducted with a mixture of coal with this solvent in an open pan, allowing free access to hydrogen at 1000 psi or higher. These experiments, although they did not show the expected heat effects, were conducted under conditions of satisfactorily low sample loss.

Intermittent Heating

Specific heat can be determined by a method of intermittent heating which allows for frequent reference to the base line. For the "substitute solvent" the results increased from about 1.6 J/gK at 300 K to about 2.8 J/gK at 500 K. For coal solvent slurries the results were about 10 percent less.

Continuous Heating

Specific heat is proportional to pen deflection and to heating rate in the case of continuous heating. The base line must be determined from a second experiment. Since the base line is seldom reproducible, this method does not give very reliable results.

The method makes possible the observation of heat effects which are superimposed on the specific heat during the first heating. Subtraction of the sensible heat, as determined in a separate experiment, makes possible the determination of the heat effect, subject to the same problems with baseline stability.

The results for specific heat showed values substantially smaller than those determined by intermittent heating. The results for heat effects in connection with dissolution or reaction were essentially negative. The processes were either too slow or involved too little heat for measurement by this method.

Conclusions

Several circumstances combine to make DSC an inadequate method for these measurements:

1. The solvent volatility is too high for measurements in an unsealed capsule. The same circumstance serves to exclude hydrogen as a reactant.
2. The sample is so small that uniformity requires fine grinding with attendant changes in character of the coal.
3. Stirring is not possible.
4. The small sample size makes auxiliary analyses, such as chemical analysis, very difficult.
5. Base-line stability, always a problem, is particularly unreliable when continuous heating over a large span is required.

DROP CALORIMETRY

The method of mixtures was used to determine the enthalpy of several samples. The apparatus was assembled for this and similar samples.

The Calorimeter

In the method of mixtures a hot sample is dropped into a cold calorimeter. The heat given up by the sample is determined by measuring the temperature change of the receiving calorimeter.

The calorimeter is shown in Figure V-1. The aluminum block weighed 8.2 kg and had a heat capacity of about 7000 J/K. It was suspended from the lid of the enclosure. Thermal isolation was improved by adding a shield of aluminum foil. The whole vessel was immersed in a constant-temperature bath maintained at 298 K. A thermistor inserted in the block was part of a bridge by means of which the temperature was determined with a sensitivity of 10^{-3} K. Two holes for receiving the sample bulbs are shown, but only one was used. The chimney extending beyond the surface of the bath was closed by a movable

FIGURE V-1. DROP CALORIMETER

radiation shield, as was the sample hole in the block. A copper thermostat served to bring the sample to a uniform temperature before the drop. A thermistor (not shown) sensed the thermostat temperature for the purpose of control. A resistance thermometer was used to determine the temperature of the sample.

Measurements

The sample was placed in a stainless steel cylinder of 40 cm³ capacity fitted with a reentrant thermometer wall. After the temperature had been stabilized the resistance thermometer was withdrawn and the sample bulb was lowered quickly into one of the holes in the aluminum block. The heated cover under the thermostat and the two radiation shields were swung aside just before the drop. The temperature of the aluminum block was observed continuously from a few minutes before the drop until an hour or more afterwards so that correction could be made for heat leaks to the block from the surroundings. The block was precooled to a starting temperature chosen so that the final temperature would be near 298 K. The heat capacity of the block was determined by dropping a sample bulb filled with water. From these measurements the heat capacity of the sample with bulb was determined. The heat capacity of the empty bulb was determined in a separate series of measurements. Calculated enthalpies were corrected for the small difference between the final temperature and 298.15 K. Some liquid vaporized while the sample was in the thermostat. The observed enthalpies should be corrected for the heat of condensation. Since neither the identity nor the amount of vaporized material was known, this correction was not made.

The results for three samples are shown in Table V-1 and in Figures V-2, V-3, and V-4. The product liquid was from the same sample also used for viscosity, density, and thermal conductivity measurements. The results have been fit to equations with the following results:

For the reference solvent,

$$H_T - H_{298.15} = 0.1134 T + 0.00247 T^2 - 253.4 \text{ J/g.}$$

TABLE V-1. ENTHALPY OF COAL LIQUIDS

Reference Solvent		Product Liquid 9/80		Slurry (S/C = 1.6)	
Temperature, K	$H_T - H_{298.15},$ J/g	Temperature, K	$H_T - H_{298.15},$ J/g	Temperature, K	$H_T - H_{298.15},$ J/g
349.6	83.1	349.6	93.8	349.7	84.9
399.8	192.4	399.2	188.1	398.8	180.7
448.1	290.9	446.1	276.8	446.8	276.4
498.8	420.8	499.0	401.3	497.9	412.5
550.0	557.5	549.5	528.8	548.7	547.2
		600.2	662.2	599.5	670.6

FIGURE V-2. ENTHALPY OF SOLVENT

Reference Temperature = 298.15 K (77 °F)

FIGURE V-3. ENTHALPY OF COAL-DERIVED PRODUCT LIQUID

Reference Temperature = 298.15 K (77 °F)

FIGURE V-4. ENTHALPY OF COAL-SOLVENT SLURRY

Reference Temperature = 298.15 K (77 °F)

Solvent/Coal = 1.62

For Product Liquid 9/80:

$$H_T - H_{298.15} = 0.3178 T + 0.00210 T^2 - 281.5 \text{ J/g.}$$

For Reference Coal Slurry (S/C = 1.6):

$$H_T - H_{298.15} = 0.0805 T + 0.00244 T^2 - 241.0 \text{ J/g.}$$

The difference between the product liquid and the slurry is less than the uncertainty in the measurements. Since the heat of reaction is presumably small, this is what one would expect. The specific heat and enthalpy values for the solvent are somewhat higher, although the difference is not great. Again, this is to be expected, since the solvent does not contain the heavier fractions and the inorganic matter, which have lower specific heats. The scatter in the results indicates an uncertainty of about 5 J/g in the reported enthalpies.

ALTERNATIVE CALORIMETER

A calorimeter capable of measuring enthalpies at the temperature of coal liquefaction and of measuring heats of reaction at such temperatures must fulfill several criteria difficult to meet:

1. It must operate at elevated pressure, say 2000 psi at least.
2. It must not keep the sample too long at these temperatures, because at these temperatures few organic compounds are stable.
3. It must be made carefully adiabatic, since radiative heat losses will be high.
4. It must allow for good chemical analysis, since both reactants and products are likely to be complex and variable.

We believe that a flow calorimeter can be built to fulfill these requirements. Liquid would be pumped through tubing leading first to a constant-temperature bath and then, guarding against heat losses, into a calorimetric bath surrounded by an adiabatic shield. Heat supplied to the

calorimeter would be just the heat required to raise the temperature of the sample from the bath temperature to the calorimeter temperature. This heat would be a measure of the heat capacity of the sample, including any reactions taking place during the heating.

If separate lines, one containing coal liquid, the other hydrogen, were brought together in the calorimeter, then, in addition to the sensible heat required to raise the temperature, the heat of reaction would be a part of the measurement. Blank runs could readily be made, or by substituting helium for hydrogen.

After passing from the calorimeter the sample would be separated into liquid and gaseous fractions and each would be accumulated and analyzed.

The calorimetric procedure outlined above requires considerable development to overcome the many difficulties. We do not see any fundamental reasons why such a calorimeter might not be developed successfully. It would provide kinetic data as well as specific heats and heats of reaction.

VI. DENSITY

Engineering calculations require a knowledge of the density of slurries and other coal liquids. The density also enters into expressions describing fluid and heat flow. Furthermore, an investigation of density leads to an improved understanding of the way in which coal interacts with solvent.

The OBJECTIVE of this task was to determine the density of several coal-solvent slurries and of preheated coal liquids through the temperature range 300 to 650 K.

The greatest difficulty in density measurements was due to the formation of gas, either from devolatilization of the coal or through vaporization of low-boiling constituents of the solvent or product liquid. It was our intention to eliminate these gases so that measurements would be made only on completely condensed samples. Since the density of gases, even at elevated pressure, is so much less, the uncertainty in the amount of gas present would make density measurement meaningless unless gases were removed. The maximum temperature for these measurements was set by this consideration. A sudden drop in density signaled the onset of gasification.

THE PYKNOMETER.

Density was measured by determining the mass of sample contained in a vessel of known volume. The apparatus is shown in Figure VI-1. A sample bulb of about 38 cm³ capacity was fitted with a reentrant thermometer well and with a 10-cm length of 1/8 in. tubing and valve. This constitutes a pycnometer which can be used up to 10 MPa (1500 psi). It can be weighed accurately on a two-pan analytical balance by overloading the balance somewhat. Several such pycnometers were used. The volume of each was determined by filling with water.

FIGURE VI-1. PYKNOMETER AND THERMOSTAT USED FOR DENSITY MEASUREMENTS

PROCEDURE

The pyknometer was filled completely with the sample to be measured. With the aid of a carefully controlled copper thermostat the sample was brought to a constant temperature. A length of 1/4 in. tubing was connected to the valve and to a nitrogen cylinder. With valves open and 7 MPa of nitrogen pressure applied, the bulb was brought to a known temperature, measured with a platinum resistance thermometer. At temperature equilibrium the valve was closed and the pyknometer was cooled. The portion of sample expelled into the connecting tube was recovered, washed with tetrahydrofuran and filtered. The pyknometer was reweighed. The procedure was then repeated at successively higher temperatures.

The weight of sample was found from pyknometer weighings. The volume was corrected for thermal expansion. These values led to the density at 7 MPa. From analysis of the small quantity expelled in each equilibration the amount of coal expelled was determined. It was found from such measurements that virtually no coal was removed in this way, so that only solvent was expelled. A correction was applied in each case to the starting solvent-to-coal ratio. Final results were adjusted for this shifting composition so that density could be shown for constant composition. A small correction was required also for the lower temperature of that portion of the sample located in the tube and valve outside the thermostat.

After each determination it was necessary to clean excess sample from the valve and to remove cleaning solvent so that the pyknometer would be clean and dry when weighed. If this was not carefully done a positive error resulted. At high temperatures gas could be generated and light oil vaporized. This caused the ejection of sample and resulted in large negative errors. The results seemed to show that both these events occurred at times.

RESULTS

Measurements were made on the solvent, on a prepared product liquid (9/80) and on two slurries having S/C ratios of 1.6 and 2.0. In addition,

several samples were subjected to mild heating under vacuum in order to draw off the lightest components and thus extend the temperature range of the measurements.

Figure VI-2 shows density, uncorrected for composition shifts, as a function of temperature for samples not evacuated prior to measurement. In order to apply a correction to yield a density curve for a slurry of constant composition, the change in density corresponding to the change in slurry composition was calculated at each temperature from the data for the two slurry samples. The ratio of the change in density to the corresponding change in the slurry composition is plotted as a function of temperature in Figure VI-3. The first two data points close to room temperature at 310 and 318 K are erroneous, presumably because the bulbs were not full when the measurements were made. The data points corresponding to 425 and 476 K also seem to indicate faulty measurements. Eliminating these four data points, a best fit straight line was drawn through the remainder to obtain the relation,

$$\frac{\Delta d}{\Delta X_g} = 0.350 T + 129 \quad , \quad (\text{VI-1})$$

where

Δd = Change in slurry density, kg/m^3

ΔX_g = Change in weight fraction coal

T = Temperature, K.

The correlation coefficient is 0.95. Equation (VI-1) was used to correct the density data for composition shifts. Figure VI-4 shows the corrected density as a function of temperature for slurries with solvent-coal ratios of 1.6 and 2.0. Table VI-1 shows the smoothed results.

For the slurry and solvent which were heated and evacuated prior to loading into the sample cell the results are shown in Figure VI-5. Comparison with Figure VI-2 shows that for the solvent, these densities are substantially higher, especially at higher temperatures. For the evacuated sample the results follow a nearly straight line up to about 550 K, after which they begin to fall off. For the unevacuated sample the results depart from a nearly straight line at temperatures above about 450 K. We do not understand the reasons for this apparent discrepancy, but we believe it is due to a real

FIGURE VI-2. DENSITY OF SOLVENT AND COAL-SOLVENT MIXTURES AS OBSERVED

The mixture was not evacuated prior to measurement.

FIGURE VI-3. RATIO OF CHANGE IN SLURRY DENSITY TO CHANGE IN SLURRY COMPOSITION FOR SAMPLES NOT EVACUATED PRIOR TO MEASUREMENT

FIGURE VI-4. SLURRY DENSITY FOR SAMPLES NOT EVACUATED PRIOR TO MEASUREMENT, CORRECTED TO CONSTANT COMPOSITION

TABLE VI-1. DENSITY OF UNTREATED SOLVENT AND SLURRIES
CORRECTED TO CONSTANT SOLVENT-COAL RATIO

Temperature, K	Density, kg/m ³		
	Solvent	S/C = 1.6	S/C = 2.0
300	1018	1126	1114
320	1003	1114	1102
340	988	1102	1090
360	973	1089	1077
380	957	1076	1063
400	941	1062	1049
420	924	1048	1034
440	906	1033	1018
460	898	1017	1001
480	869	1000	984
500	849	983	966
520	828	965	948
540	806	947	930
560	784	929	911
580	762	910	892
600	739	890	872

FIGURE VI-5. DENSITY OF SOLVENT AND COAL-SOLVENT MIXTURE

Mixtures were subjected to vacuum prior to experimentation

difference between the two samples. The difference between the two slurry runs is less, but here too the evacuated sample shows a higher density at high temperatures.

Figure VI-6 shows the results for the second prepared product liquid. A second measurement, or an evacuated sample, is also shown. The density of the evacuated sample was found to be only a little higher than that of the "as received" material. Presumably the evacuation procedure removed very little material from this sample. Although analysis showed $S/C = 2.2$, the densities are very close to the slurry densities at $S/C = 2.0$. This seems to indicate a small increase in density upon dissolution of the coal in the solvent.

APPARENT DENSITY OF COAL

Based on the assumption of additive volumes, the apparent density of coal at any temperature may be calculated from the equation:

$$\frac{1}{d} = \frac{X_s}{d_s} + \frac{(1 - X_s)}{d_1} \quad , \quad (\text{VI-2})$$

where

d = Density of the slurry

d_1 = Density of the solvent

d_s = Density of coal

X_s = Weight fraction of coal in the slurry.

The apparent density of coal was calculated by substituting the measured values of slurry and solvent densities at known compositions in Equation (VI-2). Figure VI-7 shows apparent density of coal as a function of temperature, when calculations were done with the data for samples not evacuated prior to measurements. The data points for calculations with solvent/coal ratio of 1.6 at 310, 318, 425, and 476 K show discrepancy as noted earlier.

The decrease in density to 500 K represents a coefficient of expansion of about $1.2 \times 10^4/K$, which is somewhat higher than would be expected for dry coal. The increase in apparent density above this temperature may be due to increased pore penetration related to changing viscosity and interfacial

FIGURE VI-6. DENSITY OF PRODUCT LIQUID 9-80

The solvent-to-coal ratio is about 2.2

FIGURE VI-7. APPARENT DENSITY OF COAL

The mixtures were not evacuated prior to measurement.

tension of the solvent. It has been suggested that the product liquid has a higher density than the slurry from which it was derived. One may postulate, therefore, that the increase in apparent density represents the onset of conversion, where volumes can no longer be considered additive.

Figure VI-7 shows two curves, corresponding to calculations with slurry density data, for solvent-coal ratio of 1.6 and 2.0. The calculated apparent densities differ by about 2 percent up to 575 K. The data beyond 600 K are too low on account of gas formation during measurements.

Figure VI-8 shows the apparent density of coal calculated from slurry density data for the degassed sample with a solvent/coal ratio of 2.0. The change in the calculated apparent density as a function of temperature shown in Figure VI-8 is similar to that in Figure VI-7. However, the apparent density values in Figure VI-8 are a little lower. The differences among these three results are presumably due to experimental error.

FIGURE VI-8. APPARENT DENSITY OF COAL

The mixture was subjected to vacuum prior to measurement.

VII. APPLICATION TO COAL LIQUEFACTION

An evaluation of the results from the point of view of the design engineer has been provided by Air Products and Chemicals Inc., and is reproduced as Appendix E. It was prepared before the enthalpy results by drop calorimetry had been obtained and before the analysis of viscosity data was complete.

A few of the results obtained may be of some interest in connection with other aspects of the liquefaction process, but the focus of the work has been on the preheating part of the liquefaction plant. The specific reference has been to the SRC-1 Demonstration Plant being designed by the International Coal Refining Company. However, the results should be applicable in a more general way to any preheater using caking coal and recycle solvent.

The goal of the design engineer, for which data of the kind presented here are needed, is to construct a model of the coal slurry as it passes from mix tank to reactor, through mix tank, holding tank, heat exchanger, and fired heater. The goal has not yet been met for the fired heater. The data can be applied directly to calculations for other parts of the preheating system, but not to the fired heater. The results of this work should contribute to the preparation of the needed mathematical model.

Rheology

Part III includes a discussion of the viscosity measurements and the ways in which the results were found to depend on parameters such as source of coal and solvent, solvent-to-coal ratio, particle size distribution, and time and temperature. The effect of low-temperature thickening and subsequent thinning appears to be greatly dependent on the source of coal and solvent. These effects will be felt in the mixing and holding tanks, and need to be checked for the particular materials being used. Because of the modest temperatures, this can be done with ordinary viscometers.

These results, or results of the same kind, should be found to be of direct value in design and operation of the slurry heat exchanger operating at temperatures below about 560 K (550°F). Although some viscosity increase can

occur at these temperatures, it is not likely to be significant in the short time of residence.

It is in the fired heater, operating at temperatures of 560 to 700 K (550 to 800°F) that the problems arise. The slurry passes from a Newtonian liquid to a Bingham plastic and back to a Newtonian liquid. The apparent viscosity undergoes rapid increase followed by rapid decrease. Turbulent flow changes to plug flow and back again. Designing a model seems almost hopeless. Without one it is hardly possible to predict behavior in large tubes from results obtained in small ones. The course of events may be something like the following.

At the entrance to the fired heater the flow may be turbulent, with temperature relatively constant across the pipe. At wall temperatures in the neighborhood of 560 to 580 K (550 to 585°F) the material near the wall, being at a higher temperature, begins to develop a higher viscosity and so tends to move less rapidly, while material toward the center accelerates. Further along this condition intensifies itself. The slower-moving material near the wall continues to increase in viscosity, continues to be less well mixed, and therefore continues to rise in temperature. Heat fails to move as easily toward the center, so that the discrepancy in temperatures increases. Nevertheless, heat does pass into the turbulent core so that this material too rises in viscosity. The pressure gradient increases. Further down the tube the surface temperature reaches the point at which the viscosity decreases again. The situation is now reversed. The plastic material at the center assumes plug flow while the low viscosity at the wall lubricates the flow. Soon turbulence is reestablished near the wall while heat transfer through the plug remains poor. Eventually the turbulence will penetrate to the center and the cross section will again be nearly isothermal.

This idealized picture has neglected transverse pressure gradients, which will probably result in instabilities. Thickened material may break from the wall. Pieces of gel material may be carried along in a stream of low-temperature or high-temperature liquid. Liquids of very different temperatures may be mixed. These phenomena will be greatly dependent on tube diameter. Prediction will be difficult if not impossible.

A prerequisite for modeling would seem to be the development of rate equations for the thickening and thinning processes. The data in the present study are not sufficient for this purpose. It is possible that such expressions could be derived from more extensive data.

Thermal Conductivity

The results shown in Section IV showed only small variations in thermal conductivity with temperature. The data appear to be reliable. The results are for one coal-solvent combination, however, and can be extended to material from different sources only with uncertainty. The dependence on particle size is also in need of confirmation because of the need to stop stirring some time before making the measurements.

The data seem to be adequate for application to plant design. The limitations are more in the method of heat-transfer calculation than in the data. In contrast with the viscosity measurements, these results are most reliable in the high-viscosity gel region, which is just the region in which heat transfer is mostly conductive and therefore the region in which thermal-conductivity data are most needed.

Density

The values determined here, while not extensive, are precise and reliable in the range of concentration and temperature covered.

The decrease in observed density with time, as noted in several of the viscosity determinations, is of interest in connection with a descriptive model of the changes occurring in structure. These changes in density are too small to be of major effect in connection with design problems.

Enthalpy

Drop calorimetry gives reliable values of the enthalpy. The results of the few measurements reported in Section V give usable values for the coal and solvent employed in this work. The results might be expected to depend

slightly on the source of coal and solvent. They do not depend on the solvent-to-coal ratio, apparently.

These results say nothing about the heat of reaction between coal and solvent. DSC measurements indicate no sizeable heat effect accompanying the dissolution. The heat of hydrogenation would be expected to show up at higher temperatures, not reached in these experiments. Direct measurement of the heat of reaction remains an unfulfilled need of considerable significance.

VIII. RECOMMENDATIONS

This program was conceived and carried out with application to the SRC-I Demonstration Plant in mind. The results are of far wider value, however, because of the similarity in the front end of every direct liquefaction process. In order for the results to be numerically significant they need to be broadened to include other coals and solvents. With this more universal purpose in mind the following recommendations are made:

- (1) The viscosity peak occurring as the caking coal goes into solution is by far the most significant characteristic of the thermophysical description of coal slurries in the application of this description to plant design. It is also of great importance in developing an understanding of the chemistry of liquefaction. Therefore, viscosity determinations should be expanded to include coals and solvents other than those used here. Further work needs to be done on the falling-bob method to improve its reliability and application to more concentrated slurries. An alternative form of viscometer should also be developed, especially for those high-yield-stress materials not measurable in the falling-bob apparatus. This might be some form of capillary flow instrument designed to avoid the inadequacies of a continuous-flow system.
- (2) The thermal-conductivity measurement has proven successful. The work is not entirely complete, however. Several unanswered questions need to be addressed. Is the measurement time dependent during the first few minutes after heating the slurry? In what way are the results dependent on particle size? Can the dependence on concentration be accounted for theoretically? In addition to these questions, measurements are required for other coals and solvents.
- (3) Density measurements need to be extended to higher temperatures, for which purpose sample bulbs capable of withstanding higher pressures without distortion are required. From such measurements it should be possible to generalize on the basis of densities determined conventionally at atmospheric pressure.

- (4) Enthalpy measurements need to be extended to higher temperatures to account for the effects of dissolution. These measurements had best be made in connection with high-temperature heat-of-reaction measurements in order that a more careful study of the heat of dissolution (not accessible through drop calorimetry) may be made.
- (5) The heat of reaction of coal with solvent and/or hydrogen needs to be measured. This measurement can best be made by high-temperature flow calorimetry. We know of no existing calorimeter capable of such measurements. Once the method has been developed it will be important that extensive use be made of the instrument to find the dependence of the heat effect on time, temperature, hydrogen pressure, solvent composition and, of course, on the source of the coal. Since heat production is a direct measure of reaction rate, there is much to be gained from the method beyond a determination of heat effect.
- (6) Finally, it is recommended that the government not neglect its responsibility in this area. The results are needed by all and should not be made proprietary. Private industry has demonstrated its unwillingness either to do basic work or to make available the data they do obtain.

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APPENDICES

APPENDIX A - EXPERIMENTAL PLAN FOR THERMOPHYSICAL PROPERTIES
OF COAL LIQUIDS

APPENDIX B - TIME VARIATION OF VISCOUS PROPERTIES OF
COAL SLURRIES

APPENDIX C - A TABULATION OF THERMAL CONDUCTIVITY DATA
OBTAINED IN LIQUID/COAL MIXTURES

APPENDIX D - DIFFERENTIAL SCANNING COLORIMETRY

APPENDIX E - APPLICATION OF THERMOPHYSICAL PROPERTIES
DATA FOR COAL LIQUIDS TO THE SRC-I
PROCESS AND EQUIPMENT DESIGN

APPENDIX A
EXPERIMENTAL PLAN
for
THERMOPHYSICAL PROPERTIES OF COAL LIQUIDS
October 31, 1979

SUMMARY

In this program certain thermophysical properties of coal-solvent systems are to be measured. The measurements fall into two categories. Density and specific heat are routine measurements which are anticipated to be accomplished with relatively little difficulty and in relatively short time. The other three measurements, viscosity, thermal conductivity, and heats of reaction, will be difficult to accomplish with satisfactory accuracy. Of these, the viscosity is of most immediate and compelling interest for two reasons. The viscosity changes markedly with temperature; therefore, this property spans a great range and imposes on the slurry system a very considerable variation in flow behavior. Secondly, the viscosity is of very great significance in the design of the preheater because of its relation both to flow properties and to heat transfer. Heat of reaction is also of great significance in design considerations. Few measurements of this property have been made. Thermal conductivity is also of great interest because of engineering needs and the lack of previous determinations.

While the significance of the various measurements can be ranked in the manner indicated in the previous paragraph, it will be most productive to pursue the three major problems simultaneously and to include the two minor determinations as time allows. With respect to the measurements of viscosity, thermal conductivity, and heat of reaction, it will be our intention to place major emphasis on developing reliable methods and demonstrating that accurate results can be obtained by the use of these methods. In so doing, we will postpone the investigation of some of the variables that may in the long run prove to be important. Furthermore, some variables which may be of scientific

significance will be postponed in order to concentrate on those matters of most immediate interest to engineers designing preheaters for pilot and demonstration plants.

The most immediate application of this emphasis will be in the choice of coal and solvent. Materials likely to be used in the SRC I demonstration plant being designed by APCI are chosen as the reference coal and solvent. The coal will be from a KY-9 seam, probably from the Lafayette mine. Ideally the solvent would be derived from this same coal. However a Wilsonville recycle oil derived from KY-9 coal will provide a reasonable substitute. Enough material for the program as planned will be obtained. As time permits, other related coals will be used.

More detailed plans for the experimental work, Tasks 2 through 6, are presented in subsequent sections.

Task 2 - Sample Preparation and Characterization

A reference coal, KY-9 and solvent, Wilsonville recycle oil, will be obtained through subcontractor Air Products and Chemicals, Inc. (APCI). The coal will be ground as needed by a technique that substantially excludes air and keeps the sample cold.

A reference preheater sample will be prepared from this coal and solvent using a solvent-to-coal ratio of 1.6 to 2.0 and a residence time of 5 minutes at 700 K (800°F). Four additional samples will be prepared from coals and oils to be selected after results have been obtained with the reference materials.

Reference samples will be characterized by all appropriate available methods. Other samples will be characterized wherever possible by solvent extraction.

Task 3 - Rheology Studies

The rate of temperature increase in the preheater is expected to be of the order of 1 K/sec. It will be an objective of this task to approach as nearly as possible this heating rate. However, it is recognized that the

vessel may not be heated in such a manner that any part of the sample is subjected to coking conditions. This restriction limits the rate of heating in the preheater and it may constitute the effective limiting factor in the viscometer as well.

Modifications of the viscometer will be tested with liquids of known viscosity as well as with reference coal and oil and with reference preheater sample. Subsequent to the satisfactory completion of these measurements, a meeting will be held with the DOE TPO and APCI, at which time final plans will be discussed for future measurements. It is now anticipated that the following variables will be studied in approximately the indicated order:

- Heating rate: Maximum heating rate achievable without coking up to 1 K/sec. Also slower heating rates down to 1/10 of the maximum.
- Temperature for constant temperature experiments:
 300 to 600 K: 60 K intervals.
 600 to 700: selected temperatures to study the rate of change with temperature.
 Preheater sample: 300 to 700 at approximately 80 K intervals.
- Particle size: -100 mesh to -325 mesh.
- Solvent-to-coal ratio: 1.5 to 3.0.
- Static hydrogen pressure: 7 to 20 MPa (1000 to 3000 psi).
- Solvent quality: Three or four solvents: (1) Wilsonville recycle solvent, (2) Wilsonville solvent with light end removed, (3) Wilsonville solvent with addition of light SRC fraction (from Kerr-McGee extraction process), (4) Wilsonville solvent with addition of whole SRC. Most of the work will be done with the first solvent.
- Source of coal: KY-9 coal from Lafayette mine for most of the work and other KY coals.

Work will not begin on the capillary viscometer until the modifications on the falling-cylinder viscometer are complete. This viscometer will be similar to the pipeline viscometer used at ORNL except for the method of preparing samples. It will be used as a method of comparing our results with the results obtained at ORNL. It will also provide an alternate method for comparison with results obtained by the falling-cylinder method.

Task 4 - Thermal Conductivity Measurements

Only brief design study will be attempted the first quarter, with full-scale work scheduled to begin in January, 1980. The major effort in this Task will be directed toward the design and construction of apparatus which will produce reliable data. The effect of variables is expected to be slight, so that few measurements will be required. The principal variables will be sample preparation, in that coal-solvent slurry may behave differently from preheater samples, and temperature.

Task 5 - Calorimetric Measurements

Although preliminary planning will be done before that time, experimental work is not scheduled to begin until the fifth month, i.e., February 1, 1980.

It is required that the total heat effect be determined for heating the coal-solvent slurry. The heat effect is composed of the sensible heat, that is, the specific heat multiplied by the temperature change, and the heat of reaction. Measurement of the total heat effect while the sample is heated is difficult because the calorimetry has to be done at high and constantly changing temperatures. The experimental plan is to separate the sensible heat, since this part can be measured by cooling the sample to room temperature, where calorimetry is easier. This leaves only the heat of reaction to be measured at elevated temperature.

Differential scanning calorimetry (DSC) is a technique that offers the promise of measuring both types of heat effect, but the procedure is complicated by the need for working at high pressure. There are two reasons for this need. Hydrogen must be present at high pressure, especially because it is probably necessary for any exothermic reactions to occur. Secondly, the sample must be confined so that minimal vaporization takes place, since the endothermic heat of vaporization might easily mask all other heat effects. The Du Pont DSC allows for working in an atmosphere of pressurized hydrogen

but does not suppress vaporization. There have been several attempts to work with pressurized sample containers and it now appears that some such procedure will be required.

Methods of carrying out pressurized DSC experiments will be explored during the intervening months so that experimental trials may be initiated in February. Providing that the method is successful, the following variables will be studied:

- Hydrogen pressure and hydrogen concentration: Partial pressures of hydrogen from zero to at least 7 MPa (1000 psi) will be used.
- Solvent quality: The solvent will be varied as previously described.
- Heating rate: 0.1 K/sec to 1.0 K/sec.
- Solvent-to-coal ratio: 0 to 3.
- Source of coal: KY-9 coal from Lafayette mine and other KY coals, weathered coals, coals of varying O, S, and N content.

In the event that these DSC procedures prove inadequate, other methods will be recommended. Experimental plans concerning the variables to be studied will be a part of the recommendation. The use of other methods is subject to approval by the DOE TPO.

Measurements of specific heat by the traditional method of mixtures, being physically unrelated to other calorimetric work, will be undertaken at a time when work schedules on other parts of the program allow. Three complete runs are anticipated, one on the reference solvent, one on the reference preheater sample, and one, to 600 K (620°F) only, on a coal-solvent slurry.

Task 6 - Density Measurements

Mixtures of reference solvent and reference coal in the ratio 1.6 will be heated and soaked at 550 K, 600 K, and 650 K (530, 620, and 710°F). Pyknometer densities will be measured on these materials, on the reference preheater sample, and on reference solvent at 50 K intervals. Additional measurements will be made on other preheater samples or other materials as may be required.

Table 1 shows a schedule of the experiments anticipated for the program.

TABLE 1. NUMBER OF EXPERIMENTS DESIGNED MAINLY TO DETERMINE THE EFFECT OF THE INDICATED VARIABLE

Determination	Subtask	Solvent/ Coal Ratio	Temperature of Measurement	Temperature of Sample Preparation	Heating Rate	Particle Size	Hydrogen Pressure	Solvent Quality	Source of Coal	Comparison of Methods
Viscosity										
Continuous heating	3.2.2	3		1	2	1	1	2	1	2
Constant temperature	3.2.2	3	5					2		2
Capillary viscometer	3.2.3		4							8
Thermal conductivity ^(a)	4.3	3								
Heat of reaction										
duPont DSC	5.1	6			8		4	6	6	
Improved calorimeter	5.2	6			8		4	6	6	
Specific heat by drop calorimeter ^(a)	5.3									3
Density ^(a)	6			4					4	

(a) The number of samples is shown. Each will be measured at several temperatures, representing about 15 determinations of specific heat, about 65 of density.

APPENDIX B

TIME VARIATION OF VISCOUS PROPERTIES
OF COAL SLURRIES

In this appendix a brief description of each constant-temperature measurement of coal slurries will be given, with a plot of the results. The procedure, as described in the body of the report, was to transfer cold slurry into the hot viscometer at a hydrogen pressure of 13.8 MPa (2000 psi). The temperature of the sample rose rapidly, usually to within about 1 K of the equilibrium temperature in 5 minutes. The time was reckoned from the moment of transfer. Therefore the data during the first five minutes are suspect, since the sample was at an unknown temperature.

In each case the raw data were plotted as a function of time. Cross plots were then made at selected times. These plots yielded straight lines. From the slopes and intercepts, with the aid of calibration constants and independently-determined densities, values of η_{pl} and τ_0 were found. They are the values shown on the plots in this Appendix.

The quality of the data was variable. In cases of high yield stress the uncertainty was especially high. Under more favorable conditions the data were sometimes unsatisfactory because of faulty alignment of the bob suspension. In some cases the scatter was very low and it was sometimes possible to obtain density values with good precision. Verbal indication of the quality of the data is given in the descriptions of the experiments and can usually be inferred from the plots of data.

In most cases at the conclusion of the experiment, a sample was recovered for analysis. The sample was extracted with tetrahydrofuran and the residue was ashed. This procedure leads to a value for the conversion to soluble products which does not assume that the sample recovered from the viscometer was representative of the whole quantity of product. Since the total elapsed time varied greatly from run to run, one would not expect the analytical results to be dependent on temperature and solvent-to-coal ratio alone. Much less do they represent the degree of conversion corresponding to the time at which viscosity data were obtained.

Solvent-to-Coal Ratio = 2.0A-5-1 Ratio 2.0

In this experiment the sample was loaded directly into the viscometer autoclave. The intention was to acquire data at such low temperatures as would cause little or no change in properties with time. The results are shown in Table B-1. Only the first four or five points were measured at temperatures that would meet that criterion. At higher temperatures considerable thickening took place and the data are of little value. At the conclusion, analysis showed 30.6 percent conversion to products soluble in tetrahydrofuran.

B-5-17 Ratio 2.0 (451 K, 353°F)

The sample transferred well. The data looked normal and were reasonably reproducible. The results are shown in Figure B-1. The original data indicate a slight thickening during the first few minutes. The time is too short for good precision, but the trend seems to be clearly indicated. There is some question about the temperature during the first few minutes, since the thermocouple shows the average temperature of the bulk liquid above the bob while the liquid being sheared is making good contact with the autoclave wall. Even so, the temperature of the sample is surely rising. An increasing temperature would be expected to result in a lowering of the viscosity. Therefore the initial effect seems to be real. There are two ways to calculate the yield stress. One can determine the force required to balance the bob in the liquid from the volume of the bob and the density of the slurry as determined in separate experiments. Alternatively, one can find this force from the average of two intercepts on the shear stress versus shear rate lines, the one for the ascending, the other for the descending bob. This balancing force represents the zero on the shear-stress scale. In many cases only the first method can be used, since the falling bob produces little or no data. In the present case both methods can be used, and Figure B-1 shows that the agreement is not entirely satisfactory. Conversion to soluble products was 28.2 percent.

TABLE B-1. VISCIOUS PROPERTIES OF 2.0/1 SLURRY AFTER INDEFINITE
TIME AT TEMPERATURE (13 MPa)

Temperature		Plastic Viscosity, mPa·s	Yield Stress, N/m ²
K	°F		
291.1	64.4	76.0	.41
321.2	118.4	41.6	.09
348.0	166.8	31.1	.42
373.8	213.1	17.9	.37
425.8	306.7	8.6	.44
475.2	395.6	6.6	.45
526.4	487.9	6.8	.84
501.8	443.5	9.0	.60
450.4	351.1	13.8	.40
404.0	267.4	36.2	.45

FIGURE B-1. VISCOSITY OF SLURRY B-5-17 (S/C = 2.0)
AT 451 K (353°F) AND 13.8 MPa (2000 psi) OF HYDROGEN

B-5-18 Ratio 2.0 (503 K, 446°F)

This experiment differed from others in the series in that the hydrogen pressure was maintained at 11.2 MPa (1600 psi). This lowered pressure is presumed to have had a negligible effect on the results, which are shown in Figure B-2. An initial thickening effect is seen, as in the previous experiment. After an hour and a half, a second thickening begins to occur. The values of yield stress based on these data alone agreed well with values calculated on the basis of known density. Conversion was 31.5 percent.

B-3-3 Ratio 2.0 (517 K, 471°F)

The transfer was accomplished smoothly and data were first recorded within about 2 minutes. Within about 4 minutes the temperature reached 517 K and did not vary more than about a degree thereafter. Well-formed peaks seemed to indicate smooth operation of the viscometer. However, the data were poorly reproducible, requiring the exercise of some judgment in drawing smooth curves. The final results are considered to be reliable, showing a marked thinning trend for the first 10 minutes and a very gradual thickening trend after an hour or more. The results are shown in Figure B-3. After the measurements the sample was extracted with tetrahydrofuran and the residue was ashed. This analysis leads to an estimate of 39 percent conversion into products soluble in this solvent.

B-3-6 Ratio 2.0 (528 K, 491°F)

The sample transferred well and heated rapidly to the control temperature. The data for the first 25 minutes were obtained at unnecessarily high shear rates, leading to uncertainty in interpretation. Lower shear rates were used for the remaining period, but the data scattered badly, as can be seen in Figure B-4, which shows the results. The apparent trend toward higher plastic viscosity and lower yield stress does not represent a firm conclusion in this case.

FIGURE B-2. VISCOSITY OF COAL SLURRY B-5-18 (S/C = 2.0) AT 503 K (446°F) AND 11.2 MPa (1600 psi) OF HYDROGEN

FIGURE B-3. VISCOSITY OF COAL SLURRY B-3-3 (S/C = 2.0) AT 517 K (471°F) AND 13.8 MPa OF HYDROGEN

FIGURE B-4. VISCOSITY OF COAL SLURRY B-3-6 (S/C = 2.0)
AT 528 K (491°F) AND 13.8 MPa OF HYDROGEN

B-5-20 Ratio 2.0 (531 K, 496°F)

Sample transfer was incomplete in this experiment, due to a sticking regulator. The data appeared to be excellent, but because the sample was smaller than normal there remains some question about the results, which are shown in Figure B-5. The data differ in several respects from expectations based on runs at lower and higher temperatures. The initial thickening usually observed was not evident in this case. Furthermore, one would expect gel formation and considerable thickening after an hour or so, but this was not observed. Conversion was 38 percent.

B-3-5 Ratio 2.0 (535 K, 504°F)

About 25 minutes after transfer of the sample it was concluded that the transfer had been incomplete. A second attempt was apparently successful, but it presumably disturbed the sample by introducing fresh slurry. The data peaks were not well formed and they showed excessive scatter. It is suspected that a misalignment of the system may have introduced mechanical drag. The results, shown in Figure B-6, are not considered reliable. After 90 minutes the bob stuck fast and operation could not be resumed. Conversion to soluble products was found to be 37 percent.

B-5-19 Ratio 2.0 (539 K, 511°F)

After a clean transfer, data were recorded for about 3 hours. The original data indicate qualitatively that the initial effect, for about 4 minutes, was a decided thickening. The data during these first few minutes were not sufficient for the calculation of reliable values of η_{p1} and τ_0 . Therefore Figure B-7, which shows the results, does not indicate clearly this initial effect. It does show the subsequent thinning, which persists for about half an hour, to be followed by a second thickening. This is the lowest temperature at which this second thickening has been clearly demonstrated, though it was suggested in several previous experiments. Conversion was 42 percent.

FIGURE B-5. VISCOSITY OF COAL SLURRY AT B-5-20 (S/C = 2.0)
AT 531 K (496°F) AND 13.8 MPa OF HYDROGEN

FIGURE B-6. VISCOSITY OF COAL SLURRY B-3-5 (S/C = 2.0) AT 535 K (504°F) AND 13.8 MPa OF HYDROGEN

FIGURE B-7. VISCOSITY OF COAL SLURRY B-5-19 (S/C = 2.0) AT 539 K (511°F) AND 13.8 MPa OF HYDROGEN

B-3-7 Ratio 2.0 (546 K, 523°F)

There seemed to be no marked changes with time during this experiment. The bob continued to move smoothly for about 50 minutes, when measurements were stopped. The scatter was so great as to obscure trends in the data. Therefore the lines shown in Figure B-8 are speculative.

B-3-8 Ratio 2.0 (556 K, 541°F)

After a successful transfer the first data were obtained in 5 minutes. The temperature remained within 1 degree of the mean temperature throughout the experiment. As in other measurements in this series, the scatter in the data was troublesome. However, in this case the trends were clear. The results, as shown in Figure B-9, are not highly precise, but we believe them to be reliable. After 43 minutes the bob became immobile.

B-4-11 Ratio 2.0 (566 K, 559°F)

In this and succeeding experiments a smaller bob was used. High shear rates were required to keep the bob moving. These required a correction to the data, leading to a measure of uncertainty. However, the scatter in the data was much less than in previous measurements with the larger bob. Measurements were begun about a minute after the transfer. The data showed a rapid change during the first 5 or 6 minutes. The temperature was constant after the first measurements. The bob moved freely throughout the 41-minute experiment. The results are shown in Figure B-10. Conversion to soluble products was 30 percent.

B-4-10 Ratio 2.0 (576 K, 577°F)

This experiment was qualitatively similar to that preceding. The results are shown in Figure B-11. Conversion to soluble products was found to be 35 percent.

FIGURE B-8. VISCOSITY OF COAL SLURRY B-3-7 (S/C = 2.0) AT 546 K (523°F) AND 13.8 MPa OF HYDROGEN

FIGURE B-9. VISCOSITY OF COAL SLURRY B-3-8 (S/C = 2.0) AT 556 K (541°F) AND 13.8 MPa OF HYDROGEN

FIGURE B-10. VISCOSITY OF COAL SLURRY B-4-11 (S/C = 2.0) AT 566 K (559°F) AND 13.8 MPa OF HYDROGEN

FIGURE B-11. VISCOSITY OF COAL SLURRY B-4-10 (S/C = 2.0) AT 576 K (577°F) AND 13.8 MPa OF HYDROGEN

B-4-12 Ratio 2.0 (587 K, 597°F)

The first measurements, at about 3 minutes after transfer, were at a temperature about 10 K below the final equilibrium temperature. Only after about 7 minutes after transfer was the temperature found to be constant. The sample showed signs of rapid thickening during this period. During the period from 8 to 18 minutes the bob was placed on automatic operation involving the use of a second power supply. This mode of operation has not been adequately calibrated. Furthermore, the data are sparse in this region. The data suggest that the maximum viscosity occurred after about 10 minutes. Results are shown in Figure B-12. Conversion was 37 percent.

B-4-13 Ratio 2.0 (595 K, 612°F)

After the transfer the viscosity increased very rapidly. From 5 to 15 minutes after transfer the data were unusable, partly because of the use of the uncalibrated power supply and partly because very high force was needed to move the bob, leading to high shear rates where calibration is uncertain. As in the previous experiment, temperatures were low for the first 7 minutes. When usable data were recorded again, 15 minutes after transfer, relatively reproducible values were obtained. Results are shown in Figure B-13. Conversion was 51 percent.

B-4-14 Ratio 2.0 (608 K, 634°F)

Data were recorded for 12 minutes after transfer, but both power supplies were required, and data were of poor quality. Temperature rose to the control value in about 7 minutes. After 12 minutes the bob could no longer be moved. The experiment was terminated after 19 minutes. Conversion was 41 percent.

FIGURE B-12. VISCOSITY OF COAL SLURRY B-4-12 (S/C = 2.0)
AT 527 K (507°F) AND 13.8 MPa OF HYDROGEN

FIGURE B-13. VISCOSITY OF COAL SLURRY B-4-13 (S/C = 2.0) AT 596 K (612°F) AND 13.8 MPa OF HYDROGEN

B-4-15 Ratio 2.0 (622 K, 660°F)

The bob stuck fast after about a minute and could not be freed. Therefore no data were obtained. The temperature never became constant, presumably because of the lack of stirring. Conversion was 57 percent.

B-4-16 Ratio 2.0 (652 K, 714°F)

The bob was stuck fast from 2 to 8 minutes after transfer. It subsequently moved freely at high forces and shear rates, but could not be operated slowly. Data were inadequate for reliable results, but they indicated a plastic viscosity less than 1 mPa·s and a negligibly small yield stress ($<0.2 \text{ Nm}^{-2}$). In view of the low viscosity of this sample after the first 8 minutes, it is not clear why there should have been such difficulties in making the measurements. There was no evidence of solid residue in the viscometer after the experiment. Given free bob movement, satisfactory measurements at these low viscosities requires the use of a larger bob. Conversion to products soluble in tetrahydrofuran was found to be 89 percent.

Solvent-to-Coal Ratio = 1.6D-5-4 Ratio 1.6 (449 K, 349°F)

In proposed demonstration plans the ratio of solvent to coal is to be about 1.6. Previous work in this program has been done at a solvent-to-coal ratio of 2.0 because of the difficulties in dealing with a high solids loading in the viscometer. A few measurements at 1.6 were carried out at temperatures low enough to avoid excessive thickening.

These measurements, at low temperature, were made for comparison with similar measurements at 500 K and as an aid in understanding the behavior of the slurry in the mixing tank. The experiment proceeded without difficulty. The results are shown in Figure B-14. The initial thickening is rapid, even at this low temperature, but is slow enough to allow reasonably successful data taking. Therefore the changes in both η_{pl} and τ_0 are well defined. A comparison with experiment B-5-17 (Figure B-1), in which a more dilute

FIGURE B-14. VISCOSITY OF COAL SLURRY D-5-4 (S/C = 1.6) AT 449 K (349°F) AND 13.8 MPa (2000 psi) OF HYDROGEN

mixture was used, shows the same pattern of behavior, but substantially higher values of both η_{pl} and τ_0 . Conversion to soluble products was found to be 8.6 percent.

D-5-1 Ratio 1.6 (500 K, 440°F)

These measurements at 500 K proceeded smoothly. The results are shown in Figure B-15. The initial thickening effect appears here as a rise in the yield stress. The second thickening also appears in the yield-stress results, a change that is hardly detectable. A comparison may be made with Figure B-2, showing results for the more dilute slurry at a slightly higher temperature. Both plastic viscosity and yield stress are much higher in the case of the Ratio 1.6 experiment. The initial thickening appears in the more dilute case as a rise in plastic viscosity. This contrast may be an artifact of data treatment, since the data were never adequate in the first few minutes of the experiment. At the conclusion the conversion was found to be 20 percent.

D-5-6 Ratio 1.6 (513 K, 464°F)

Results are shown in Figure B-16. 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. Conversion was 20 percent.

D-5-3 Ratio 1.6 (525 K, 485°F)

Because of the difficulties encountered at 550 K, an attempt was made to make measurements at 525 K. At first the data peaks were distorted, indicating too rapid a movement of the bob. Later the shape of the peaks became more nearly normal, but the measurements were not reproducible. Two approximate results were obtained as follows:

FIGURE B-15. VISCOSITY OF COAL SLURRY D-5-1 (S/C = 1.6) AT 500 K (440°F) AND 13.8 MPa (2000 psi) OF HYDROGEN

FIGURE B-16. VISCOSITY OF COAL SLURRY D-5-6 (S/C = 1.6) AT 513 K (464°F) AND 13.8 MPa of HYDROGEN

After 15 min $\eta_{pl} = 23 \text{ mPa}\cdot\text{s}$; $\tau_0 = 4.1 \text{ N/m}^2$;

After 45 min $\eta_{pl} = 16 \text{ mPa}\cdot\text{s}$; $\tau_0 = 5.2 \text{ N/m}^2$.

At these values of yield stress the material does not flow like an ordinary viscous liquid. Rather, the solids tend to be segregated from a fluid part of the sample. At the conclusion of the experiment one third of the sample was recovered from the top of the bob in the form of a paste. The experiment was repeated (D-5-5) with the addition of a baffle plate just above the surface of the liquid. The results were similar but of higher quality. Conversion was 19 percent.

D-5-5 Ratio 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 to be remixed with the liquid. This expediency was partly successful and the data are shown in Figure B-17. The data for plastic viscosity were not very reproducible, probably due to fluctuations in the distribution of solids in the liquid phase. Conversion was 35 percent.

D-5-2 Ratio 1.6 (550 K, 530°F)

An attempt was made to make measurements at this coal concentration at 550 K. The mixture stiffened rapidly to the extent that no measurements could be made. By increasing the power applied to the lifting magnet, it was possible to continue stirring, but no useful data could be obtained. After an hour the temperature was reduced and it was found to be possible to operate the instrument again at lower temperatures. A cake of solid material was found on the bob after disassembly. Conversion was 24 percent.

FIGURE B-17. VISCOSITY OF SLURRY D-5-5 ($S/C \approx 1.6$) AT 525 K (486°F) AND 13.8 MPa OF HYDROGEN

Solvent-to-Coal Ratio = 2.6G-5-1 Ratio 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 B-18. The data seemed reasonably satisfactory. It was possible to make a determination of density, and these results are shown also in Figure B-18. Conversion was 24 percent.

G-5-3 Ratio 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 B-19.

Comparison with a similar run at a lower temperature (G-5-1) (Figure B-18) 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. Conversion was 34 percent.

G-5-4 Ratio 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 $3.8 \text{ mPa}\cdot\text{s}$ was estimated, with a yield stress of about 0.9 N/m^2 . After about 2 hours lower values were observed, $1.7 \text{ mPa}\cdot\text{s}$ and 0.1 N/m^2 . 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. Conversion was 41 percent.

FIGURE B-18. VISCOSITY OF COAL SLURRY G-5-1 (S/C = 2.6) AT 540 K (513°F) AND 13.8 MPa OF HYDROGEN

FIGURE B-19. VISCOSITY OF COAL SLURRY G-5-3 (S/C = 2.6) AT 552 K (534°F) AND 13.8 MPa OF HYDROGEN

G-5-5 Ratio 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 B-20. During the first 5 minutes there appeared to be a rapid thickening, but the data were not sufficient for calculation of the parameters η_{p1} and τ_0 .

Solvent-to-Coal Ratio = 3.0F-5-1 Ratio 3.0 (540 K, 512°F)

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 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 B-21. 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 B-21. We were surprised to find the declining values of the density, but the data seem to show it clearly. Conversion was 27 percent.

FIGURE B-20. VISCOSITY OF COAL SLURRY G-5-5 (S/C = 2.6) AT 577 K (579°F) AND 13.8 MPa OF HYDROGEN

FIGURE B-21. VISCOSITY OF COAL SLURRY F-5-1 (S/C = 3.0) AT 540 K (512°F) AND 13.8 MPa OF HYDROGEN

Coarse Grind CoalD-5-7 Coarse Grind, Ratio 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 B-22, 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 B-14 shows that the sample with the finer grind showed greater viscosity. Conversion was found to be 37 percent, though this seems high.

G-5-2 Coarse Grind, Ratio 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 B-23. Although the uncertainties are great, comparison with G-5-1 (Figure B-18) shows that the results, also at this temperature, are dependent on particle size. Conversion was 62 percent.

FIGURE B-22. VISCOSITY OF COARSE COAL SLURRY D-5-7 (S/C = 1.6) AT 450 K (350°F) AND 13.8 MPa OF HYDROGEN

FIGURE B-23. VISCOSITY OF COARSE COAL SLURRY G-5-2 (S/C = 2.6)
AT 540 K (512°F) AND 13.8 MPa OF HYDROGEN

Other Coal and Solvent

E-5-1 Fort Lewis Solvent and Coal,
Ratio 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 B-24.

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/m². Conversion was found to be 12 percent.

FIGURE B-24. VISCOSITY OF FORT LEWIS SLURRY E-5-1 (S/C = 1.6) AT 451 K (352°F) AND 13.8 MPa OF HYDROGEN

E-5-3 Fort Lewis Coal and Solvent,
Ratio 2.6 (540 K, 513°F)

These measurements also were made with coal and solvent obtained from The Pittsburg and Midway Coal Mining Company. Results are shown in Figure B-25. 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 B-18 and B-26 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. Conversion was 24 percent.

E-5-2 Fort Lewis Coal, Reference Solvent
Ratio 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 B-26 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 fall in measured density seems very large. One would expect the density to remain nearly constant. Conversion was 21 percent.

FIGURE B-25. VISCOSITY OF FORT LEWIS SLURRY E-5-3 (S/C = 2.6) AT 540 K (513°F) AT 13.8 MPa OF HYDROGEN

FIGURE B-26. 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

APPENDIX C

A TABULATION OF THERMAL CONDUCTIVITY
DATA OBTAINED IN LIQUID/COAL MIXTURES

TABLE C-1. 1.6:1 SOLVENT TO COAL MIXTURE THERMAL CONDUCTIVITY
DATA OBTAINED ON 8/26/80

Run No.	Gage Resistance* Ω	Gage Current mA	Temperature K	Measured Thermal Conductivity W/mK
1	15.38	59.9	298	.157
2	15.48	59.7	300	.158
3	22.04	58.6	424	.146
4	24.27	57.9	466	.138
5	27.78	57.2	550	.126
6	29.22	57.0	583	.124
7	31.34	56.6	619	.114
8	31.23	56.6	618	.126

* Gage length = 7.26 cm

TABLE C-2. 1.6:1 SOLVENT TO COAL MIXTURE THERMAL CONDUCTIVITY
DATA OBTAINED ON 10/30/80

Run No.	Gage Resistance* Ω	Gage Current mA	Temperature K	Measured Thermal Conductivity W/mK
1	13.62	57.2	282	.160
2	17.62	-	367	- **
3	17.68	-	369	- **
4	19.85	-	414	- **
5	21.94	55.3	460	.155
6	21.94	55.3	460	.150
7	21.94	55.4	460	.148
8	25.17	54.8	528	.137
9	25.36	54.8	532	.135
10	25.81	54.8	535	.139
11	29.74	-	632	- **
12	29.48	53.7	634	.113
13	29.64	53.7	638	.108
14	30.60	53.8	652	.093
15	30.77	53.8	656	.096
16	31.28	53.7	670	.095
17	31.48	53.7	674	.091
18	31.48	53.7	674	.092

* Gage length = 7.26 cm

** No thermal conductivity data

TABLE C-3. 2:1 SOLVENT TO COAL MIXTURE THERMAL CONDUCTIVITY
DATA OBTAINED ON 7/23/80

Run No.	Gage Resistance* Ω	Gage Current mA	Temperature K	Measured Thermal Conductivity W/mK
1	16.05	60.0	297	.149
2	16.11	59.9	298	.147
3	20.64	58.9	380	.146
4	20.64	58.9	380	.145
5	23.52	58.3	434	.138
6	25.94	57.7	485	.134
7	26.02	57.7	480	.136
8	27.91	57.3	520	.131
9	29.96	57.0	563	.128
10	33.41	56.3	628	.098/.081

* Gage length = 7.86 cm

TABLE C-4. 3:1 SOLVENT TO COAL MIXTURE THERMAL CONDUCTIVITY
DATA OBTAINED ON 10/16/80

Run No.	Gage Resistance* Ω	Gage Current mA	Temperature K	Measured Thermal Conductivity W/mK
1	14.62	56.2	288	.148
2	14.62	56.2	288	.146
3	16.34	56.0	322	.145
4	18.09	55.5	356	.141
5	18.09	55.5	356	.146
6	19.79	55.2	392	.145
7	19.84	55.2	392	.136
8	21.92	54.6	434	.132
9	21.92	54.8	434	.136
10	21.99	54.4	434	.137
11	21.99	54.5	434	.134
12	21.99	54.5	434	.138
13	21.99	54.5	472	.134
14	23.58	54.5	472	.134
15	23.58	54.3	511	.130
16	25.37	54.0	511	.129
17	25.37	53.8	545	.128
18	26.90	54.2	586	.112
19	26.90	54.2	586	.109
20	30.21	53.2	622	.111
21	30.21	53.2	622	.110
22	30.31	53.1	623	.107
23	31.25	52.9	647	.097
24	31.29	52.9	648	.096
25	32.74	52.7	678	.095
26	32.74	52.7	678	.094
27	32.70	52.6	678	.095
28	33.46	52.5	693	.098
29	33.48	52.5	694	.096
30	34.20	52.4	707	.094
31	34.16	52.4	706	.094

* Gage length = 7.58 cm

TABLE C-5. PRODUCT LIQUID THERMAL CONDUCTIVITY
DATA OBTAINED ON 6/30/80, 7/1/80

Run No.	Gage Resistance* Ω	Gage Current mA	Temperature K	Measured Thermal Conductivity W/mK
1	16.70	60.0	298	.137
2	16.66	60.0	298	.138
3	16.68	60.0	298	.136
4	16.70	60.0	299	.136
5	18.39	59.6	328	.143
6	18.32	59.6	327	.143

* Gage length = 7.86 cm

TABLE C-6. PRODUCT LIQUID THERMAL CONDUCTIVITY
DATA OBTAINED ON 9/17/80, 9/18/80

Run No.	Gage Resistance* Ω	Gage Current mA	Temperature K	Measured Thermal Conductivity W/mK
1	15.22	59.8	298	.146
2	15.22	59.8	298	.144
3	17.38	59.3	334	.142
4	19.01	59.0	372	.139
5	21.01	58.4	409	.130
6	21.01	58.2	412	.130
7	23.27	58.1	453	.130
8	23.31	58.0	454	.129
9	25.12	57.6	488	.129
10	25.12	57.6	490	.129
11	27.11	57.2	527	.118
12	27.21	57.3	529	.118
13	28.90	56.8	562	.110
14	29.19	56.8	568	.109
15	30.62	56.6	598	.100
16	30.86	56.5	602	.098
17	14.54	60.0	285	.140
18	14.54	60.0	285	.140
19	22.40	58.3	435	.127
20	28.97	57.0	564	.111
21	28.97	57.0	564	.110
22	32.91	56.0	647	.105
23	33.09	56.0	649	.100
24	33.09	56.0	649	.098
25	35.42	54.7	687	.093
26	35.42	55.3	687	.095

* Gage length = 7.26 cm

TABLE C-7. SOLVENT THERMAL CONDUCTIVITY DATA
OBTAINED ON 6/16/80

Run No.	Gage Resistance* Ω	Gage Current mA	Temperature K	Measured Thermal Conductivity W/mK
1	16.55	59.9	294	.126
2	16.54	59.9	294	.127
3	18.05	59.5	320	.123
4	18.10	59.5	320	.125
5	19.73	59.2	350	.121
6	21.78	58.7	388	.118
7	21.83	58.6	388	.116
8	24.10	58.4	432	.112
9	24.16	58.4	433	.109

* Gage length = 7.26 cm

TABLE C-8. SOLVENT THERMAL CONDUCTIVITY DATA
OBTAINED ON 9/15/80, 9/16/80

Run No.	Gage Resistance* Ω	Gage Current mA	Temperature K	Measured Thermal Conductivity W/mK
1	15.18	61.7	293	.119
2	15.18	61.7	293	.123
3	16.40	59.6	318	.113
4	19.09	58.9	373	.111
5	21.41	58.5	419	.106
6	21.41	58.5	419	.109
7	14.77	60.2	288	.119
8	18.99	59.1	372	.114
9	23.16	58.2	458	.104
10	23.16	58.1	458	.098
11	24.63	57.9	490	.101
12	24.63	57.9	490	.098
13	26.33	57.5	526	.102
14	26.46	57.5	529	.095
15	28.24	57.1	570	.101
16	28.40	57.0	571	.097
17	28.40	57.0	571	.095
18	30.57	56.2	617	.096

* Gage length = 7.26 cm

TABLE C-9. SOLVENT THERMAL CONDUCTIVITY DATA
OBTAINED ON 10/29/80

Run No.	Gage Resistance* Ω	Gage Current mA	Temperature K	Measured Thermal Conductivity W/mK
1	14.21	57.0	286	.128
2	14.21	57.0	286	.129
3	29.50	53.9	601	.090
4	29.50	53.9	601	.089
5	31.89	53.5	647	.093
6	31.89	53.5	647	.087
7	33.64	53.0	689	.084
8	33.64	53.0	689	.081
9	34.06	53.0	699	.084
10	34.06	53.0	699	.082

* Gage length = 7.26 cm

APPENDIX D

DIFFERENTIAL SCANNING CALORIMETRY

The Calorimeter

The objectives of this task were:

- To determine the specific heat of the solvent and the coal-solvent mixture as a function of temperature
- To obtain quantitative data on the energy change involved in dissolution reactions when the coal-solvent mixture is heated in hydrogen atmosphere.

A Du Pont Pressure Differential Scanning Calorimeter (DSC) was used for this purpose.

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 block 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. The gas enters the cell base and is preheated by circulation through the block before entering the sample chamber at block temperature. 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 specific heat and the rate of temperature increase.

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.

Specific Heat Determination

The specific heat of a test specimen is determined by comparing the thermal lag between sample and reference systems under blank and sample conditions. During the blank run both sample and reference pans are empty. The experiment is repeated under identical conditions with a weighed sample in the sample pan. With the temperature of the silver block held constant, the temperature of the sample is measured with a high-precision potentiometer. The temperature of the system is raised 10 or 20 degrees, then held constant for a second temperature measurement. During the heating period the difference thermocouple generates a peak, the area of which is proportional to the heat transferred to the sample. The area of the peak is determined by drawing a line from the point where the thermogram departs from the baseline to the point where it returns, and measuring the enclosed area with a planimeter. The measured peak area in in.^2 under blank and sample conditions is converted to mv min from the recorder chart speed and the span used. The difference is computed at each temperature of interest. Specific heat of the sample is then calculated from the equation:

$$Q = mC_p\Delta T = AK \quad , \quad (D-1)$$

where

Q = Total heat supplied to raise sample temperature by ΔT , joules

m = Mass of the sample, g

C_p = Sample specific heat, J/gK

ΔT = Sample temperature rise, K

A = Peak area converted to mv min and corrected for run under blank condition

K = Cell calibration constant at the temperature of interest, J/mv min.

Equation (D-1) gives the average sample specific heat over ΔT .

By choosing small increments of temperature rise, the specific heat of the specimen is determined over the entire temperature range of interest.

Alternatively, the specific heat may be determined directly from the pen deflection and the rate of temperature rise, but with reduced accuracy due to uncertainty in the baseline.

Determination of the Cell Calibration Constant

The value of the calibration constant was determined by running a standard material of known specific heat (Al_2O_3) under the same conditions as the unknown sample and substituting the values of m , C_p , ΔT and A in Eq. (D-1). In order to ensure accuracy in measuring the peak areas, the planimeter was calibrated by measuring known areas on the chart paper.

Determination of the Specific Heat of Solvent

A high boiling range coal-derived solvent was used to minimize loss of solvent by vaporization during heating. The material, a "solvent substitute", was provided by Air Products and Chemicals. A weighed amount of the solvent was placed in an aluminum pan provided with a covering lid. A small hole was made in the lid with a #80 drill and the sample was encapsulated with an encapsulating press. The hole in the lid was provided to allow hydrogen to pressurize the sample and to equalize the pressure. The empty reference pan was similarly sealed with the same size hole in the center of the lid. The cell was slowly pressurized to 5.27 MPa (750 psig). After allowing time for temperature stabilization, the sample was heated in small increments, holding the temperature constant at the end of each increment until the baseline on the recorder stabilized. The cell pressure increased gradually to 6.65 MPa (950 psi) as the sample was heated to 540 K. The peak areas were measured with the planimeter and the specific heat calculated from Eq. (D-1). After depressurizing and cooling to ambient conditions, the cell was opened and the sample pan weighed again. A 2.8 percent sample weight loss was observed, although there were no visible signs of sample loss through the hole in the

lid. The observed loss in weight could be attributed to vaporization of low boiling fractions in the solvent. In order to determine the magnitude of the effect caused by the loss of low boiling fractions on the specific heat measurements, the sample pan was returned to its position on the DSC cell and measurements repeated over the same temperature range. Figure D-1 shows specific heat as a function of temperature. A smooth curve is drawn through the data points for the two solvent runs. The results indicate that the data from the two runs agree fairly well, and that the observed sample weight loss did not significantly affect the specific heat measurements. The sample pan was weighed after the second experiment. The uncertainties above 500 K are due to early difficulty in temperature control caused by excessive heat losses.

Specific Heat of Coal-Solvent Mixture

A mixture of Kentucky No. 9 coal and the high boiling solvent was prepared such that the weight ratio of solvent to coal was 1.6. A weighed amount of this mixture was placed in the sample pan and covered with the lid. The lid had a hole (made by a #80 drill) at the center. After a blank run with empty pans, the sample pan was loaded and sealed with the encapsulating press and specific heat measurements were carried out as in the case of the solvent. The reference pan used was the same one used during calibration. After depressurizing the cell and cooling to ambient conditions, the sample pan was weighed. A 2.2 percent weight loss was observed. The sample pan was returned to its position on the DSC cell and the measurements repeated. The sample weight loss after the second experiment was less than 1 percent. The results for the two runs are plotted in Figure D-1. The results are comparable to those shown in Section V from drop calorimetry.

Discussion of Results

The substitute solvent is a solid at room temperature. When heated in the presence of nitrogen at near atmospheric pressure, the solvent melts in the range of 340 to 360 K (158 to 194°F) and loses some volatile matter around 470 to 500 K (387 to 440°F). Heating the solvent under pressure in hydrogen

FIGURE D-1. SPECIFIC HEAT OF SOLVENT SUBSTITUTE AND SLURRY
IN HYDROGEN ATMOSPHERE (5.27 to 6.65 MPa)

minimizes loss of sample by vaporization but does not significantly change the temperature range over which the solvent melts. Therefore, the specific heat values reported in Figure D-1 include the heat of melting of the solvent and the heat of vaporization of the volatile components involved during the heating process. These heat effects appear to be small.

In the case of the coal-solvent mixture, there is some difference in the data points for the two runs on the same sample. This difference may be due to change in mixture composition resulting from loss of volatile components. It may also be due to some chemical reaction between the coal and the solvent under the conditions involved, or the partial dissolution of the coal in the solvent, both of which will result in a test specimen different from the original specimen.

It is evident from Figure D-1 that there is a wider scatter in the data beyond 500 K. The method of measurement by the DSC cell assumes that the heat supplied is transferred to the sample and reference pans primarily through the constantan discs supporting the pans. At higher temperatures a portion of the supplied heat is dissipated through hydrogen, which is a good thermal conductor. Above 500 K (440°F), the system could not be operated under automatic control, and so the sample temperature was maintained constant at the end of each temperature increment by manual adjustments. Temperatures higher than 550 K could not be reached on account of heat losses. This was true also for the calibration run.

Because of the inability to control temperatures at even so low a temperature as 500 K, it was necessary to make several modifications to the DSC apparatus. The insulation between the furnace and the pressure containment was improved. The power supply was adjusted to make more power available. The control instrument was overhauled and readjusted. All of this resulted in the necessary improvements in performance.

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 mixture at a constant rate of about

22 degrees/min from room temperature to 438°C. The instrument was calibrated for continuous operation, for which the appropriate equation is:

$$\frac{dQ}{dt} = m C_p = \frac{KY}{dT/dt} \quad . \quad (D-2)$$

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 help resolve the difficulty. Since the study of coal-solvent slurries had higher priority, no further attempts were made to find reasons for the disagreement.

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 the hole in the lid), and prevent coal-solvent reactions. To ascertain if this was true, 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 the DSC cell 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 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 the equation:

$$E = \frac{K \Delta Y}{m H_R} \quad (D-3)$$

where

E = Net energy evolved or absorbed by reaction between coal and solvent per degree per unit weight of starting material, J/gK

K = Cell calibration constant, J/mv min

ΔY = Difference between pen deflections during the first and second runs on the same sample, mv

H_R = Heating rate, °/min

m = Mass of the sample at the start of the first run, gm.

Discussions of Results

Figure D-2 shows the net energy evolved or absorbed due to reaction, as 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 D-2:

- 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 is probably due to loss of water. The exothermic effect may not 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. The result is an apparent exotherm on the difference plot (Figure D-2). The endotherm, if the effect is real, may be due to melting of a component formed from the interaction of coal and solvent or derived from the inorganic matter in the coal.

Determination of Energy Change for Mixtures with Other Coals

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

6-D

FIGURE D-2. 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)

1. Kentucky Nos. 9 and 14 supplied by Pittsburgh 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 D-3 through D-5 show the net energy evolved or absorbed for these mixtures. In the case of the Kentucky Nos. 9 and 14 coal-preheated solvent mixture (Figure D-3), it is evident that the general shape of the curves from repeat experiments are 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 solvent mixture (Figure D-2). In the case of the mixture with Ohio coal (Figure D-4), the exothermic effect appears to cover a wider range of temperature. This may or may not be true because a shift 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 D-5) behaves differently.

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, using the second runs in each case. The appropriate equation for calculating specific heat from continuous heating operation is:

$$C_P = \frac{K (Y_2 - Y')}{m H_R} \quad (D-4)$$

where

C_P = Specific heat of the mixture, J/gK
 K = Cell calibration constant, J/mV min

FIGURE D-3. NET ENERGY EVOLVED OR ABSORBED AS A FUNCTION OF TEMPERATURE FOR KENTUCKY NOS. 9 AND 14 COAL - PREHEATED SOLVENT SLURRY IN HYDROGEN ATMOSPHERE (5.67 to 6.65 MPa)

FIGURE D-4. 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 D-5. 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)

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

Y' = Pen deflection with empty pans on both platforms

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

H_R = Heating rate, K/min.

Equation (D-4) gives the specific heat with reduced accuracy due to uncertainty in the baseline. Figures D-6 through D-8 show calculated specific heats for the different coal-solvent mixtures. Comparing Figures D-1 and D-5, it appears that specific heat calculated from Eq. (D-4) gives lower values than Eq. (D-1). The general scatter in the specific heat data in all cases is probably due to the uncertainty in the baseline.

Conclusions

It may be concluded that the Du Pont DSC cell is useful to obtain qualitative information on the type of heat effects produced when coal-solvent slurries are heated in hydrogen atmosphere. However, reproducibility in the quantitative data generated by the techniques described above is inadequate partly because of baseline shifts and partly because of the impossibility of confining the sample and providing at the same time a controlled atmosphere.

FIGURE D-6. SPECIFIC HEAT AS A FUNCTION OF TEMPERATURE FOR KENTUCKY NO. 9 COAL-SUBSTITUTE SOLVENT SLURRY IN HYDROGEN ATMOSPHERE (5.27 to 6.65 MPa)

D-16

FIGURE D-7. 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 D-8. SPECIFIC HEAT AS A FUNCTION OF TEMPERATURE FOR OHIO COAL-PREHEATED SUBSTITUTE SOLVENT SLURRY IN HYDROGEN ATMOSPHERE (5.27 to 6.65 MPa)

APPENDIX E

APPLICATION OF THERMOPHYSICAL PROPERTIES DATA FOR
COAL LIQUIDS TO THE SRC-I PROCESS AND EQUIPMENT DESIGN

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The experimental program planned for this project was determined in accordance with the expected needs for the engineering design of the coal slurry heating system in the SRC-I process. The particular goal of these studies was to provide data in support of the slurry fired heaters and the interpretation of heat transfer and pressure drop data to be obtained from the pilot plants at Wilsonville and Fort Lewis. In the event, the data was also found to be of value in the design of the slurry heat exchangers preceding the fired heater.

Viscosity

Prior to these measurements it was known that the viscosity varied widely as the slurry was heated from 350°F to 800°F. Peak viscosity was indicated to be in the temperature range from 550-650°F by batch autoclave experiments conducted by Gulf and in-line viscosity experiments at Oak Ridge National Laboratory and a minimum viscosity was expected to occur at from 400-500°F.

In general the results confirmed this expected pattern. The majority of the data have been obtained in more dilute slurries than the plant design (i.e., at a solvent to coal ratio of 2). The measured viscosities have been correspondingly low. Measurements at the design solvent to coal ratio of 1.6 have given higher viscosities such that measurements could not be completed at temperatures above 500°F.

Shallow viscosity minima can be deduced from the results in the temperature zone 350 to 500°F. Serious slurry thickening is not apparent until temperatures exceed 500°F. The importance of this is to confirm the

selection in the SRC-I process design of a 500°F transition temperature from the slurry heat exchanger to the slurry fired heaters.

A second important observation has been the Bingham plastic characteristic of the flow. Recognition of this has allowed correlation of viscosity data observed in mixing experiments at Fort Lewis. (*) Comparison of the Fort Lewis and present data show some discrepancies in magnitude, with the Fort Lewis values being approximately 200 to 400% of the Battelle values in the temperature range 350 to 400°F. Both results have been taken into account in determining the heat transfer and pressure drop for the design of the slurry heat exchanger.

The viscosity measurements have been of less value in the analysis of fired heater data. The complexity of the fluid mechanics has prevented rigorous analysis of the heat transfer mechanism and it has been necessary to use empirical correlation techniques which have not required viscosity data.

Thermal Conductivity

Prior to these measurements, only estimates of thermal conductivity were available. The results obtained have been used directly in specifying the design of the slurry heat exchangers for the Demonstration Plant.

The measured data have not been used directly in the calculation of the fired heater because of the empirical correlation techniques adopted for heat transfer. However, the data is valuable in demonstrating that thermal conductivity discontinuities do not exist and that the substantial variations observed in Fort Lewis heat transfer data must result from variation in the system fluid mechanics.

Density

The density data have given good confirmation of design estimates and have been used directly for both the analysis of pilot plant data and the design of the Demonstration Plant.

(*) SRC-I Quarterly Technical Report, April-June 1981.

The increase in the apparent density of coal at around 500°F again confirms the selection of 500°F as the transition temperature from slurry heat exchanger to fired heater.

Specific Heat

Heat capacity of the solvent-coal mixture has proved to be particularly difficult to measure at conditions representative of the fired heater. However, it is of direct importance in determining the duty requirements of the fired heater and heat exchangers. Initial design estimates were found to be low in comparison with data measured in a separate program by Wilco Research Co. (*) Thus, the data obtained here were of particular interest as an independent check. The scatter in the results and the limitation on maximum temperature achieved do not permit direct verification; however, the reported specific heats are comparable to those measured by Wilco.

Further studies are desirable in this area and the development of techniques to measure heat of reaction would be especially valuable in the temperature range 700 to 850°F.

(*) SRC-I Quarterly Technical Report, January-March 1980.