

APPENDIX C

VISCOSITY AND DENSITY
OF H-COAL PDU LIQUID SLURRY SAMPLES:
BATTELLE INSTITUTE FINAL REPORT

FINAL REPORT

on

VISCOSITY OF H-COAL SAMPLES

to

AMOCO OIL COMPANY

June 30, 1981

by

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and S. P. Chauhan**

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VISCOSITY OF H-COAL SAMPLES

by

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ABSTRACT

The rheological properties of 14 samples taken from the H-COAL pilot plant have been determined at temperatures up to 725 K (845 F), mostly at a pressure of 17.24 MPa (2500 psia) of hydrogen. The samples showed Bingham-plastic behavior. It was found that the properties were time-dependent in that the yield stress decreased to near zero. The rate of this change was higher at higher temperatures. Most measurements were made without regard to this time dependency. Therefore the results at the highest temperatures are somewhat in doubt for this reason.

INTRODUCTION

On December 11, 1979, Battelle submitted its report to AMOCO on measurements made on a few H-COAL samples. On April 25, 1980, we submitted our proposal for more measurements and the current program got under way on September 18, 1980.

The objective of this research was to determine the rheological properties of 15 samples to be supplied by AMOCO. The samples were to be collected without exposure to air and were to be transferred into our apparatus without exposure to air. Measurements were to be made of a suitable range of shear rates at temperatures between 350 and 450 °C under hydrogen pressures of 2000 to 3000 psi.

It was not expected that the properties would change appreciably with time, but the possibility was recognized. Therefore measurements were begun at lower temperatures and continued at higher temperatures until the series was complete. With some of the samples repeat measurements were made

at lower temperatures after completing the high-temperature work. Some of the samples were maintained for a while at one temperature to check on the constancy of results. It became apparent that the results were indeed time-dependent. Since extensive constant-temperature measurements with extrapolation to zero time would have required large samples and a lot of time, only one such measurement was made in this manner, by way of illustration.

RHEOLOGY

Most of the work on rheology 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 particles.⁽¹⁾ Coal-oil suspensions made with brown coal have been found to increase in viscosity with aging, even at room temperature.⁽²⁾ 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 viscosity.⁽⁵⁾

A few attempts have been made to measure viscosity at elevated temperature and pressure. In a continuing program at Oak Ridge National Laboratory a continuous coal-liquids flow system has been instrumented for measurement of viscosity and density.⁽⁶⁾ 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.

Viscometer

A reciprocating concentric-cylinder viscometer was developed at Battelle for measuring the viscous properties of Synthoil liquids at elevated temperature and pressure.⁽⁷⁾ It seemed well suited for the present

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 sample mixed. Data can be obtained quickly. The bob can be operated over a wide range of shear rates.

The apparatus is shown in Figure 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, can be used to hold 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 the 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 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 brazed 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 three-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

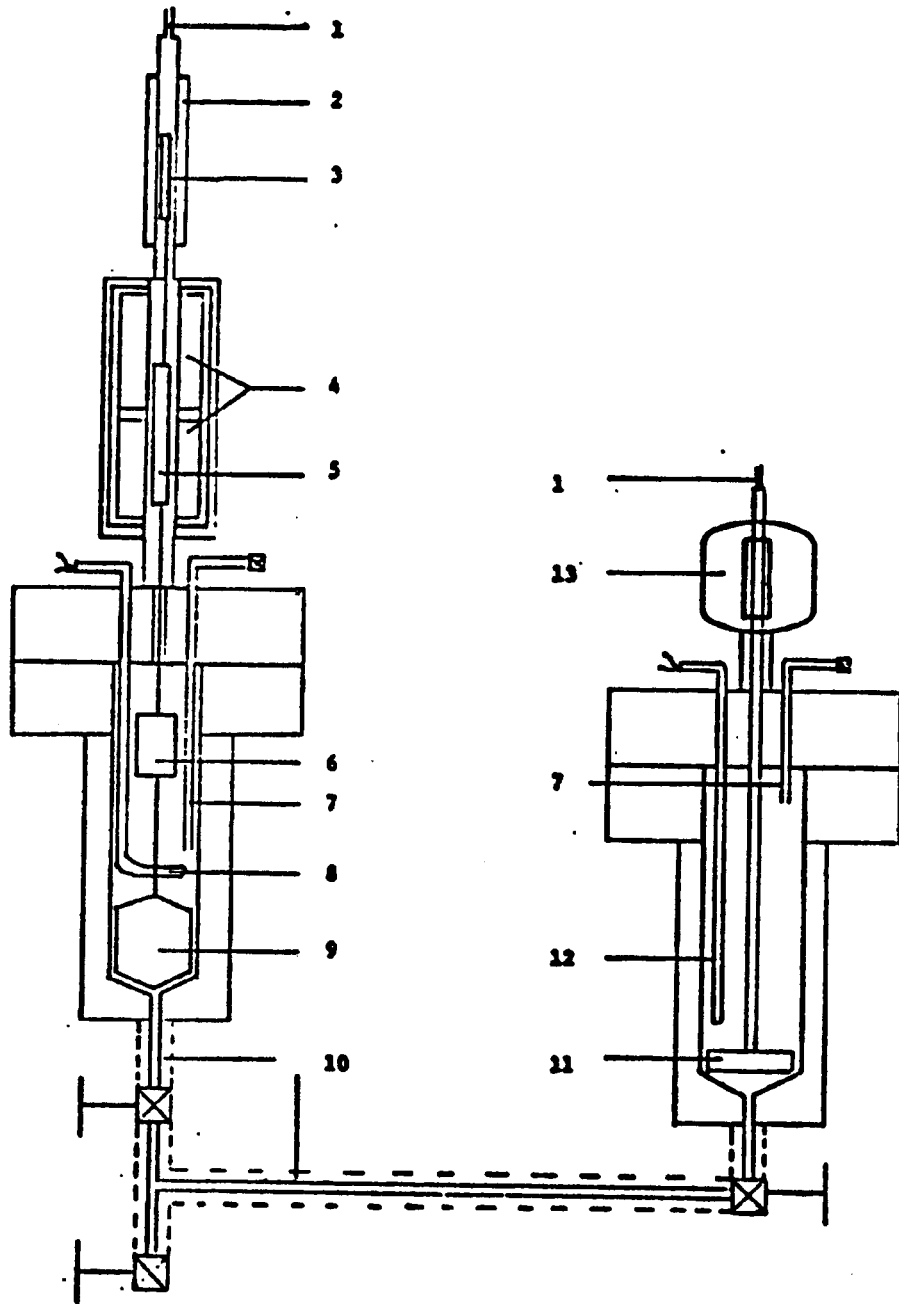


FIGURE 1. VISCOMETER AND MIXING AUTOCLAVE

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-in. 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 back-pressure 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.

Procedure

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.^(7,8) The force applied to the bob was derived by calibration from the current passed through the lifting coils. From this calibration and from the dimensions of the apparatus the current scale could be converted to a shear-stress scale. 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 liquids not departing greatly from Newtonian behavior, the zero on the shear-stress scale could be estimated from data obtained with both a rising and a falling bob. From this value and from a knowledge of the volume of the bob, the density could be calculated. Shear rate was related to bob velocity through a calibration with a Newtonian standard.

Figure 2 shows a sample plot of shear stress versus shear rate. A force equivalent to about 3.65 on the shear-stress axis was required to overcome gravity in this instance. Two sets of points are shown, one for

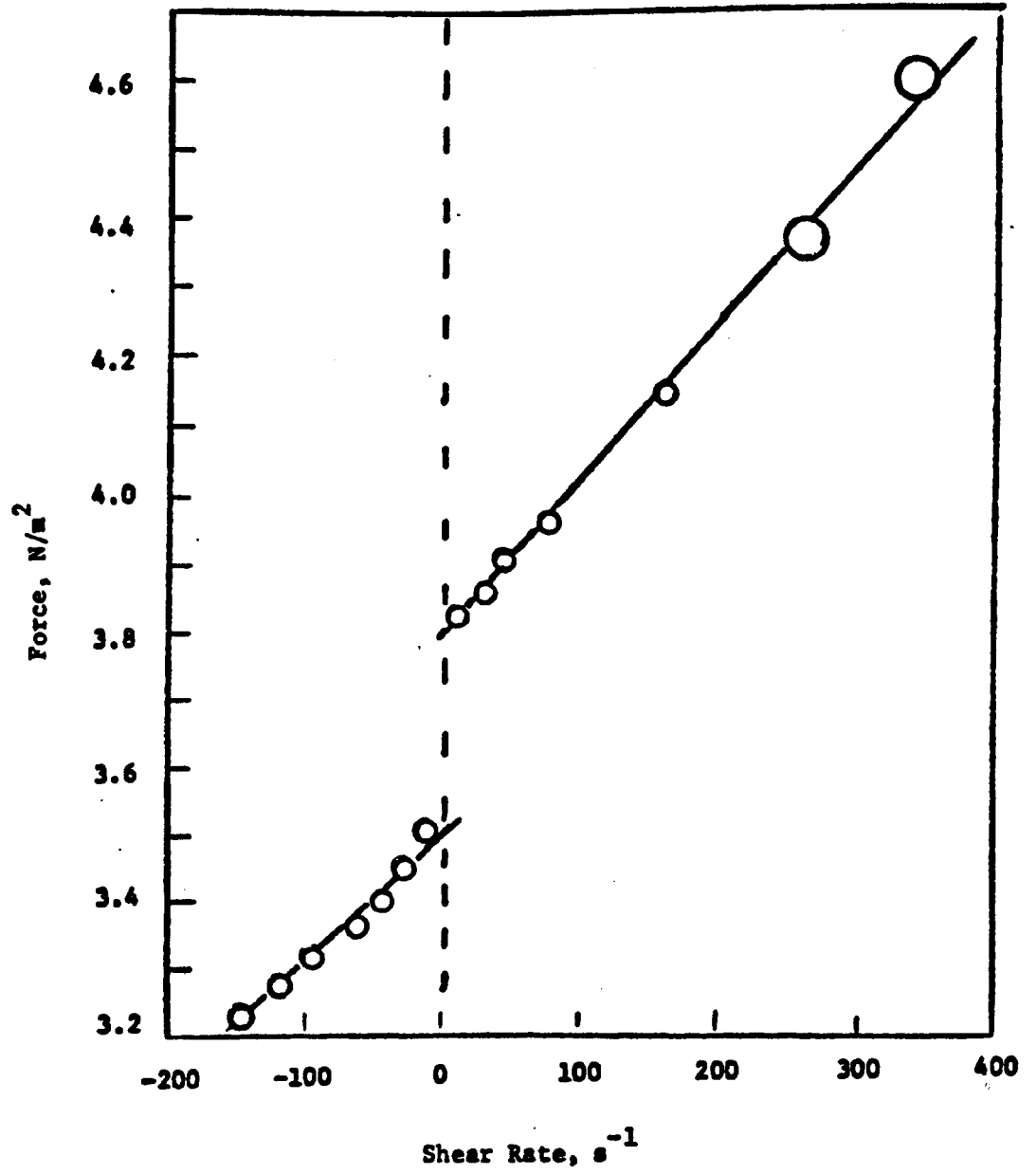


FIGURE 2. SAMPLE DATA

a rising, the other 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:

$$\tau = \tau_0 + \eta_{pl} \dot{\gamma}, \quad (1)$$

where τ_0 is the dynamic stress and η_{pl} is the "plastic viscosity", that is, that is, the slope of the line of Figure 2. The self-centering behavior of the bob works better on the rising stroke, therefore, results were based mostly on the upper line. Most of the data were obtained at shear rates between 10 and 100 s^{-1} .

When good data were obtained both with a rising and a falling bob, the point on the stress axis corresponding to a balanced bob could be determined (3.65 in Figure 2). This corresponds to a determination of the weight of the bob immersed in the liquid. A similar determination for the bob suspended in air and a determination of the volume of the bob are all that are needed for a density determination. This procedure was used for the density determinations shown. The procedure was not very successful at 400 K but appeared to give reliable results at higher temperatures.

The procedure for loading samples into the viscometer was as follows. The AMOCO sample bulb, wrapped with heating tape and insulation, was mounted vertically beside the apparatus shown in Figure 1. The valves at the bottom were connected with 1/4-in. tubing. The valve at the top of the sample bulb was connected to a low-pressure hydrogen supply and to a vent through a bubbler. Both autoclaves were first evacuated and flushed with hydrogen. After warming the sample to about 350 K the pressure in the sample bulb was relieved. Then a stream of hydrogen was passed up through the sample to provide some mixing.

The transfer was begun by applying a small pressure (about 20 psig) to the top of the sample bulb as well as to the mixing autoclave, opening connecting valves, then bleeding gas slowly from overflow tube 7 in the mixing autoclave. When the liquid level reached the overflow tube the flow of gas stopped and the connecting valve below this autoclave was closed. Hydrogen was then passed from the viscometer autoclave into the mixing autoclave to clear the connecting tube. The mixing autoclave now contained about 300 cm^3 of sample, a little more than three times as much

as the required sample. The charge was stirred vigorously for a time to homogenize the sample. Sample was then transferred in a similar way into the viscometer until it rose to the level of overflow tube 7 in this autoclave. Excess sample was blown out this overflow tube, thus leaving a sample of the required volume in the viscometer. Unused sample from the mixing autoclave was then transferred back into the sample bulb where it was kept with an overpressure of about 50 psig of hydrogen.

Before beginning the measurements the pressure in the viscometer was increased to the desired level, then the temperature of the viscometer was raised to the temperature chosen for the first measurements. After making the necessary measurements, the viscometer and contents were raised to the next higher temperature until the work was completed. At the conclusion of the measurement the sample was drained from the autoclave and discarded.

On several occasions we departed from the standard procedure, either intentionally or out of necessity. The exceptions will be described by sample number:

- AMOCO 1, 2, and 3. For these samples the pressure was increased and decreased throughout the run in an attempt to find the effect of pressure. These pressure changes were not made at the highest temperatures for fear of losing volatiles with the venting gas.
- AMOCO 3. Because of the formation of a plug in the transfer line, it was not possible to return sample to the sample bulb. The sample used for the measurements was subsequently removed through the top of the viscometer and, after exposure to air, was returned to the sample bulb.
- AMOCO 7. This was the sample chosen for our first measurements. We developed a plug during the first attempt to transfer. The sample was contaminated with air and water and some of it was evaporated after overheating. After the measurements we had trouble draining the sample and damaged our bob, which had not been properly calibrated. Therefore this run was declared to be a total loss.
- AMOCO 8. At the end of the second run with this sample we judged that no unused sample remained in the mixing autoclave. We therefore transferred the sample used for the measurements back into the sample bulb.

- AMOCO 12. There appeared to be insufficient sample for a full charge to the viscometer although apparently normal data were obtained. The sample was returned to the sample bulb after the measurements.
- AMOCO 13. We could find no sample in this bulb. Therefore, we presume the sample bulb now to be empty.
- AMOCO 15. In order to make one good observation of the effect of time on our results, a second measurement was made with this sample using a modified procedure. The overflow tube 7 in the mixing autoclave was lengthened so that a sample of the required size could be introduced into this autoclave. After making this transfer the autoclaves were both pressurized to 17.24 MPa (2500 psi) and the viscometer (but not the mixing autoclave) was heated to 700 K. The cold sample was then transferred to the preheated autoclave where it was heated rapidly to the measurement temperature. Data were recorded at 700 K for an hour and a half. Subsequently measurements were made at lower temperatures.
- AMOCO 16. We apparently encountered a plug in the line and found transfer difficult. We were unable to return sample to the sample bulb and presume that the sample bulb is now empty.

The viscometer, which had been performing acceptably at higher viscosities, gave data with a lot of scatter with these specimens. Presumably this was due to frictional effects, which represent a much more serious problem at low viscosities than at higher. During January, 1981, we made some vigorous attempts to correct these frictional problems.

For our bob to move up and down within the autoclave without friction requires good alignment. We had been relying on a flexible joint which allowed the bob to center itself in the autoclave even if the magnet assembly was not perfectly aligned. During January we made the following changes:

- (1) A tool was devised which enabled us to align the axis of the magnet housing accurately with the axis of the autoclave
- (2) One of the guides which kept the magnet assembly running true was removed. This eliminated one possible source of friction.

- (3) The flexible joint was replaced with a fixed connector.
- (4) The system was calibrated over the range of 0.3 to 33 mPA·s (cP).

The calibrations, which were based on the known viscosities of five liquids, were in satisfactory agreement. The scatter in the measurements on coal liquids was greatly reduced.

We believe that the older data, while flawed by excessive scatter, were otherwise valid. However the quality of data improved, beginning with AMOCO 4, run in late January, and subsequent determinations will be considered more reliable. Most of the measurements made prior to that time were subsequently repeated.

Results

The results of our measurements are shown in Table 1. Within each set of measurements on a single sample the results are shown in the order in which they were obtained. In most cases the first measurement was made at about 400 K. This routine was established in order to show gross differences from sample to sample, since measurements are more easily made at higher viscosities. The results show that there was the expected relationship between viscosities at lower and at higher temperatures, but there were also many departures from this relationship.

The accuracy of these results is plainly not high. It is difficult to place a numerical estimate on the uncertainty. Perhaps the best assessment would come from the numerous repeat determinations and comparisons with work at ORNL. These comparisons will be discussed in a subsequent section.

In almost all cases the data followed the relationship corresponding to Bingham plastic behavior. At low shear rates, of the order of 10 s^{-1} , shear rates often appeared to be higher than the Bingham-plastic straight line would predict. This may be an artifact of the measurement or it may indicate that the true behavior is somewhere between pseudo-plastic and Bingham plastic.

TABLE 1. VISCOUS PROPERTIES OF AMOCO SAMPLES

Temperature		Pressure		Elapsed Time, min	Viscosity η_{pl} mPa·s	Yield Stress, τ_0 N/m ²	Density, kg/m ³
K	°F	MPa	psia				
<u>AMOCO 1 (March)</u>							
408.2	275.0	17.24	2500		10.4	.20	1065
625.5	666.1	13.79	2000		2.07	.05	909
624.9	665.1	17.24	2500		2.15	.04	907
625.2	665.6	20.69	3000		2.03	.03	901
648.5	707.5	13.79	2000		1.87	.06	881
649.2	708.8	17.24	2500		1.87	.05	884
648.9	708.3	20.69	3000		1.84	.04	882
673.2	752.0	20.69	3000		1.77	.08	858
673.5	752.5	17.24	2500		1.77	.08	858
673.2	752.0	13.79	2000		1.71	.08	862
699.2	798.8	17.24	2500		1.73	.09	828
724.0	843.4	17.24	2500		1.33	.13	766
673.2	752.0	17.24	2500		1.84	.06	832
<u>AMOCO 1 (November)</u>							
413.4	284.4	17.24	2500		8.8	.13	1033
623.5	662.5	13.79	2000		1.76	.06	900
624.3	664.0	17.24	2500		1.72	.02	899
624.8	664.9	20.69	3000		1.72	.01	897
645.3	701.8	13.79	2000		1.45	.12	869
645.7	702.5	17.24	2500		1.63	.13	870
646.2	703.4	20.69	3000		1.46	.11	870
669.2	744.8	13.79	2000		1.81	.12	856
698.2	797.0	17.24	2500		1.55	.08	818
723.2	842.0	17.24	2500	4	1.28	.16	762
722.7	841.1	17.24	2500	18	1.68	.24	755
723.1	841.8	17.24	2500	26	1.87	.32	750
723.2	842.0	17.24	2500	34	2.03	.33	755
<u>AMOCO 2 (May)</u>							
406.6	272.3	17.24	2500		16.6	.26	1080
626.2	667.4	↓	↓		2.10	.10	913
648.2	707.0	↓	↓		1.92	.13	895
672.4	750.7	↓	↓		2.01	.15	844
672.2	750.2	↓	↓	37	1.92	.13	849
697.4	795.6	↓	↓	67	1.81	.20	804
725.0	845.2	↓	↓	97	1.76	.20	763
<u>AMOCO 2 (December)</u>							
405.2	269.6	17.24	2500		14.0	.31	1107
627.0	668.8	13.79	2000		2.18	.07	925
627.2	669.2	17.24	2500		2.07	.05	932
626.6	668.3	20.69	3000		1.98	.09	926
646.0	703.2	13.79	2000		1.57	.11	903
646.6	704.3	17.24	2500		1.82	.13	899
648.2	707.0	20.69	3000		1.91	.09	900
672.4	751.1	17.24	2500		1.38	.17	865
696.2	793.4	17.24	2500		1.60	.18	836
719.6	835.7	17.24	2500		1.53	.23	798
<u>AMOCO 3 (March)</u>							
409.0	276.4	17.24	2500		80.2	2.0	
627.0	668.8	13.79	2000		5.81	.42	995
627.3	669.4	17.24	2500		5.53	.42	996
627.2	669.2	20.69	3000		5.60	.42	1000
627.4	669.6	17.24	2500		5.23	.35	985
622.7	661.1	13.79	2000		5.22	.37	993
649.5	709.3	13.79	2000		5.00	.39	979
650.2	710.6	17.24	2500		4.97	.38	977

TABLE I. (Continued)

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Temperature		Pressure		Elapsed Time, min	Viscosity η_{pl} mPa-s	Yield Stress, τ_0 N/m ²	Density, kg/m ³
K	°F	MPa	psia				
<u>AMOCO 3 (March)</u> (Continued)							
650.0	710.2	20.69	3000		4.94	.35	973
673.4	752.4	20.69	3000		3.58	.32	944
673.2	752.0	17.24	2500		3.52	.29	941
672.8	751.3	13.79	2000		3.70	.28	945
699.0	798.4	13.79	2000		2.95	.22	911
699.0	798.4	17.24	2500		2.65	.20	905
699.0	798.4	20.69	3000		2.77	.18	900
723.2	842.0	17.24	2500		2.20	.14	875
699.1	798.6	17.24	2500		2.11	.07	902
409.6	277.5	17.24	2500		46.3	.00	1093
<u>AMOCO 4 (May)</u>							
407.6	274.1	17.24	2500	0	44.5	1.52	1069
622.2	660.2	↓	↓	80	3.46	.22	968
646.6	704.3	↓	↓	120	3.13	.22	952
646.2	703.4	↓	↓	190	3.11	.18	950
672.2	750.2	↓	↓	230	2.78	.15	925
698.2	797.0	↓	↓	250	1.85	.16	896
722.7	841.2	↓	↓	280	1.72	.08	863
722.8	841.5	↓	↓	288	1.60	.07	865
722.6	841.1	↓	↓	316	1.31	.00	859
722.6	840.9	↓	↓	345	1.32	.01	861
722.6	840.9	↓	↓	381	1.31	.01	860
<u>AMOCO 4 (January)</u>							
407.2	273.2	13.79	2000		31.8		
626.2	667.6	↓	↓		3.65	.18	958
649.2	708.8	↓	↓		3.51	.18	942
673.6	752.7	↓	↓		2.78	.20	922
697.4	795.7	↓	↓		2.12	.20	896
722.4	840.7	↓	↓		1.74	.09	887
<u>AMOCO 5 (February)</u>							
408.2	275.0	12.41	1800		73.0		
623.6	662.9	13.10	1900		3.49	.10	981
647.4	705.6	↓	↓		2.66	.11	971
673.2	752.0	↓	↓		2.62	.07	946
698.7	797.9	↓	↓		2.38	.06	924
722.7	841.1	↓	↓		2.19	.06	897
<u>AMOCO 6 (February)</u>							
408.5	275.5	17.24	2500		197		
623.7	662.9	↓	↓		3.26	.42	1032
647.2	705.2	↓	↓		4.93	.40	1021
670.5	747.1	↓	↓		4.46	.32	995
697.4	795.6	↓	↓		3.42	.26	966
723.2	842.0	↓	↓		2.30	.08	938
<u>AMOCO 8 (April)</u>							
407.2	273.2	17.24	2500		20.8	.60	1071
621.6	659.3	↓	↓		4.20	.15	960
648.2	707.0	↓	↓		3.96	.14	938
672.2	750.2	↓	↓		3.78	.18	917
699.2	798.8	↓	↓		3.67	.15	877
724.2	843.8	↓	↓		2.59	.08	844
698.6	797.9	↓	↓	0	2.32	.02	864
698.2	797.0	↓	↓	50	2.16	.02	855
697.6	796.1	↓	↓	80	2.40	.00	865
698.2	797.0	↓	↓	120	2.33	.00	849

TABLE 1. (Continued)

Temperature		Pressure		Elapsed Time, min	Viscosity η_{sp} MPa·s	Yield Stress, τ_0 N/m ²	Density, kg/m ³
K	°F	MPa	psia				
<u>AMOCO 8 (December)</u>							
352.2	174.2	17.24	2500		147		
416.6	290.3				17.1	.53	1092
625.4	666.0				3.30	.25	969
649.2	709.0				3.77	.22	953
672.2	750.2				2.58	.21	923
696.6	794.1				2.41	.15	910
725.0	845.4				2.20	.16	883
<u>AMOCO 9 (April)</u>							
407.8	274.3	17.24	2500		19.9	.38	1076
624.0	663.4				3.25	.14	956
648.2	707.0				2.60	.14	940
674.4	754.2				2.30	.12	916
699.2	798.8				1.82	.09	881
725.2	845.6				1.81	.04	844
700.2	800.6			0	1.19	.00	850
700.6	801.5			25	1.10	.00	848
701.2	802.4			40	1.15	.00	844
701.4	802.8			55	1.15	-.01	843
701.2	802.4			70	1.09	-.01	841
<u>AMOCO 9 (December)</u>							
407.4	273.6	17.24	2500		24.0	.48	1120
626.2	667.4				2.71	.25	930
648.8	708.3				2.15	.28	919
650.0	710.4				3.35	.31	912
672.6	750.9				2.33	.34	895
695.6	792.3				2.55	.37	800
695.8	792.7				3.24	.36	881
717.0	830.8				1.80		
<u>AMOCO 10 (April)</u>							
408.4	275.5	17.24	2500		37.2	1.03	1121
625.6	666.5				3.61	.18	963
648.6	707.9				3.25	.16	937
677.0	758.8				3.01	.13	915
700.6	801.5				1.92	.12	877
724.6	844.7				1.74	.10	838
699.4	799.3			0	1.42	.01	852
699.6	799.7			34	1.31	.01	866
699.2	798.8			63	1.20	.00	864
698.2	797.0			91	1.22	-.01	865
698.8	798.3			137	1.24	.00	865
<u>AMOCO 10 (January)</u>							
407.0	273.0	17.24	2500		31.0	.53	1122
625.0	665.4				2.08	.18	965
649.2	708.8				1.92	.16	935
673.6	752.7				1.60	.13	917
697.0	794.8				1.64	.12	884
725.4	846.0				1.10	.17	870
<u>AMOCO 11 (February)</u>							
409.7	277.7	17.24	2500		31.0	.23	1244
620.2	656.6				4.92	.48	1028
649.4	709.2				4.43	.47	1011
672.7	751.1				3.88	.46	990
697.9	796.9				2.95	.41	965
721.4	838.8				2.23	.23	938

TABLE 1. (Continued)

Temperature		Pressure		Elapsed Time, min	Viscosity η_{pl} mPa·s	Yield Stress, τ_0 N/m ²	Density, kg/m ³
K	°F	MPa	psia				
<u>AMOCO 12 (February)</u>							
408.2	275.0	17.24	2500		18.4	.49	1067
723.7	662.9				2.81	.08	950
647.7	706.1	↓	↓		2.25	.10	931
672.7	751.1				1.94	—	(906)
698.5	797.5				(2.05)	.11	890
723.5	842.5	↓	↓		1.58	.06	873
<u>AMOCO 14 (March)</u>							
411.2	280.4	17.24	2500		24.7	1.41	1096
624.0	663.4				1.77	.08	978
647.8	706.3	↓	↓		1.47	.08	949
673.4	752.4				1.18	.05	928
698.0	796.6				.89	.01	897
724.3	844.0	↓	↓		.74	.00	864
<u>AMOCO 15 (March)</u>							
410.0	278.2	17.24	2500		96.3	.76	1190
626.1	667.2				6.74	.38	1031
650.0	710.2	↓	↓		5.24	.26	1002
674.3	754.0				3.53	.21	975
697.6	795.9				2.88	.18	947
723.3	842.2	↓	↓		2.13	.06	928
<u>AMOCO 15 (June)</u>							
353.2	176.0	17.24	2500	0			
702.0	805.0			8	4.66	.54	989
694.0	790.0	↓	↓	11	3.74	.51	986
702.6	805.1			18	3.85	.41	978
700.2	800.8			28	3.52	.29	972
702.6	804.9			36	3.24	.24	969
701.2	802.4			60	2.77	.14	955
701.6	803.1			75	2.73	.10	950
702.8	805.3			85	2.73	.08	948
704.0	807.4			100	2.81	.06	941
677.6	760.1			135	2.84	.04	955
649.0	708.6			220	3.12	.04	976
623.4	662.5	↓	↓	257	3.61	.05	988
<u>AMOCO 16 (March)</u>							
408.7	275.9	17.24	2500		59.9	.88	1220
623.7	662.9				4.92	.11	1028
648.2	707.0	↓	↓		4.14	.11	1012
673.5	752.5				3.49	.11	994
698.5	797.5				2.54	.05	966
724.0	843.4	↓	↓		2.11	.04	956

The plastic viscosity was found to decrease as the temperature increased, as expected. The relationship between yield stress and temperature was not so clear. As will be shown in the next section, the yield stress at any high temperature was found to decrease with time. Therefore a decrease in yield stress with increasing temperature, as was generally observed, may have been due in part to change with time. Nevertheless, there did seem to be some decrease of yield stress with increasing temperature. This effect was relatively small, however. The determination of yield stress at 400 K was not very reliable because of the higher viscosities and the uncertainty in the density.

Changes with Time

The program was devised with the assumption that the samples would not change appreciably with time. It was recognized, however, that changes were possible. Therefore measurements were made as rapidly as possible, starting at lower temperatures and continuing at higher temperatures. In several cases (1, 3, 8, 9, 10) measurements at a lower temperature were repeated after completing the high-temperature work to determine whether any changes had occurred. It was found that both lower plastic viscosities and lower yield stress values were measured after holding at a higher temperature.

On several occasions we held the specimen for a while at constant temperature to determine whether the properties were constant. In general (8, 9, 10) we found a slight decrease in plastic viscosity and a decrease in yield stress. The yield stress at 700 K after previous measurements at 725 K were already low, but they appeared to decrease essentially to zero. AMOCO 1 appeared to be an exception to this behavior. After half an hour at the highest temperature, both plastic viscosity and yield stress were increasing.

At the end of the program, with the opportunity for one more experiment, it was determined to devote this one experiment to a determination of the changes with time at a single temperature. AMOCO 15, previously measured in March, was chosen for this experiment. The sample

was transferred from an autoclave at 353 K to the viscometer at about 700 K. Measurements began immediately but it took about 8 minutes to bring the sample to this temperature. The behavior at 400 K is shown in Figure 3.

The decrease in plastic viscosity seems to be clearly indicated, though the apparent upturn at the end is not so certain. The yield stress changed in a much more pronounced way, decreasing nearly to zero in less than 2 hours. At 425 K the change would, no doubt, be more rapid. The change in density was unexpected. The change was about 5 percent, which is a substantial change. The data seem to indicate this change clearly. We are not sure what to make of it.

The data obtained during sample heatup, while not sufficient for treatment in the usual way, indicate a thickening of the sample, whether caused by an increase in plastic viscosity or an increase in yield stress is not clear. This time period was difficult to interpret because rising temperatures were changing density and therefore buoyancy of the bob. Therefore we cannot be sure about this apparent transitory phenomenon.

One more peculiarity in the data should be pointed out. For AMOCO Samples 1 and 2 the trend with time and for yield stress even with temperature seems to be the reverse of that generally observed. Each sample was run twice, and in each of the four runs there appears to be an upward trend in yield stress.

Effect of Pressure

For several samples measurements were made at pressures of 13.8, 17.2 and 20.7 MPa of hydrogen. No discernible trend was detected. Previous experience with similar but much more viscous materials indicates that the pressure effect might have been expected to be about 5 percent for a 1000 psi change -- higher viscosity for the higher pressure. The scatter in our data was often greater than that.

Replication

In all, six of the determinations were repeated. The scatter was great, even after the January corrections. Furthermore, in most cases the earlier results in plastic viscosity were consistently lower than the later. The average difference between the earlier and later determinations ranged from 11 percent for AMOCO 1 to 36 percent for AMOCO 10. Sample 1 is said to be the same as Sample 2; similarly Samples 8 and 9 were duplicates. Each of these four was run twice. The deviations between the pairs in each case were of the same order of magnitude as deviations between repeat runs.

A similar comparison between repeat determinations of yield stress shows a similar level of agreement. At higher temperatures the agreement is worse, presumably as the yield stress decreased with time for each measurement.

In general we would have to say that the agreement between repeat determinations was less good than we had hoped. This is only partly due to uncertainties regarding the condition of the sample, such as the possible separation of solids before transferring the sample to the viscometer, uncertainties in the extent of change brought about by standing at high temperature and the like. A large part of the uncertainty seems to be due to instrumental problems such as the lack of alignment.

Comparison with ORNL Results

It is our understanding that the correspondence of samples used by ourselves and ORNL is as shown in Table 2. Because of the changes with time we have shown also our yield stress results at 700 K, which we judge to be closer to the value at zero time than the value determined at 725 K.

Although the order of magnitude of the results was the same as determined by the two methods, the agreement is not very close. Especially in the case of AMOCO 11 and Sample 43A the results are in serious disagreement, even in density. Because of the rapidity of changes with time, which is no doubt greater at 725 K than shown in Figure 3 at 700 K, and because of the differences in residence time for the two methods, the differences

TABLE 2. COMPARISON OF RESULTS AT 725 K

<u>ORNL Results</u>				
Sample Number	27B	34A	42A	43A
η_{pl} , mPa·s	1.68	3.03	1.73	1.07
τ_o , N/m ²	.126	.307	.232	.192
ρ , kg/m ³	908	985	882	851
<u>This Research</u>				
Sample Number	5	6	9	11
η_{pl} , mPa·s	2.19	2.30	1.81	2.23
τ_o at 725, N/m ²	.06	.08	.04	.23
τ_o at 700, N/m ²	.06	.26	.09	.41
ρ , kg/m ³	897	938	844	938

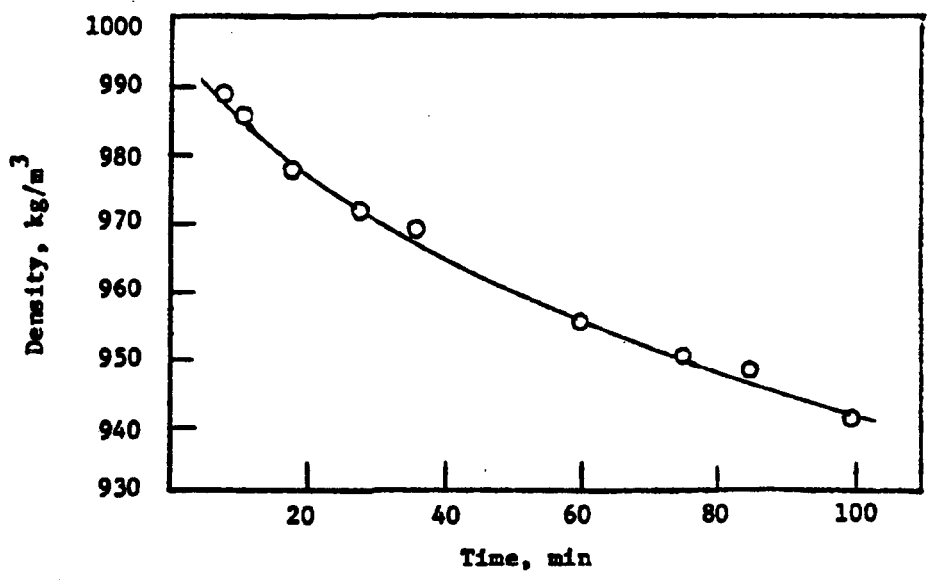
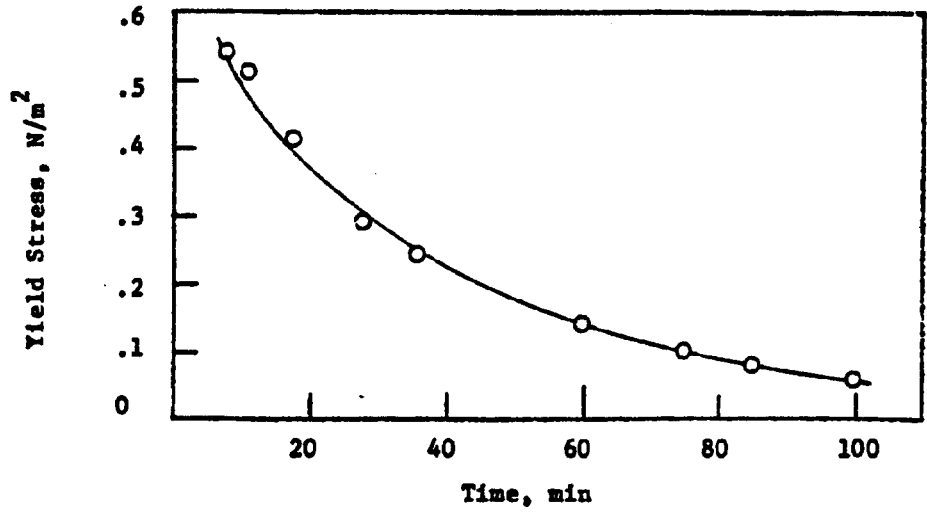
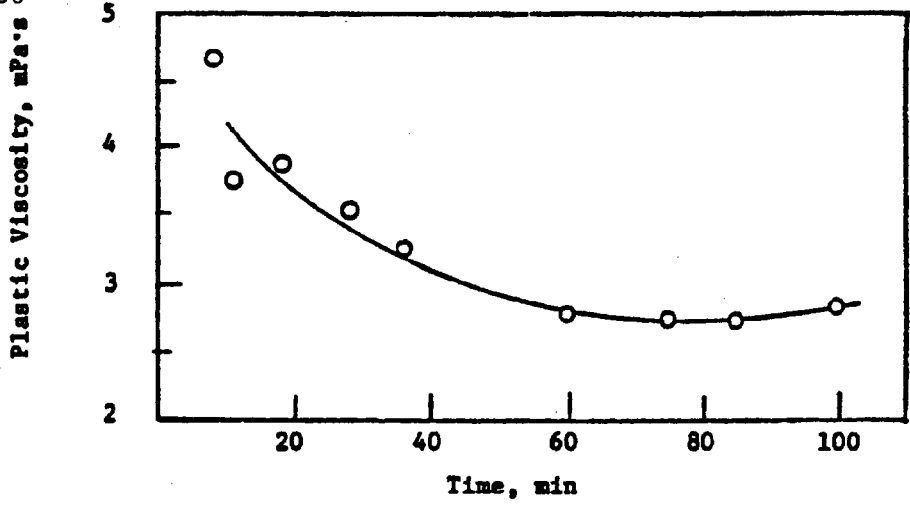


FIGURE 2 VISCOSITY PROPERTIES OF AMOCO 15 AT 700 °F

in results were perhaps no greater than should be expected. Even so, the differences between 11 and 43A seem to be excessive.

FUTURE WORK

Further determinations of rheological properties of samples such as those examined in this program would have to be based on an experimental design that deals with the changes in properties with time. Experiments similar to the one illustrated in Figure 3 could be used to extrapolate results back to zero time. With a little practice we believe that usable results could be obtained within 2 or 3 minutes of the transfer. Similar measurements at other temperatures would aid in interpretation of the results.

Further development of the instrument, together with some stable samples with which to make comparisons, should lead to greater confidence in the results.

REFERENCES

- (1) Castillo, C. and Williams, M. C., "Rheology of Very Concentrated Coal Suspensions", Chem. Eng. Commun., (3), 529-547 (1979).
- (2) Bhattacharya, S. N. and Barro, L., "Rheology of Aging of Coal-Oil Suspensions", Rheology (Proceedings of 8th International Congress), 1980, 2, 615-621.
- (3) Krzyzanowska, T. and Marzec, A., "Coal-Derived Group Component Effects on Viscosity", Fuel, 57, 804-805 (1978).
- (4) Bockrath, B. C., Lacount, R. B., and Noceti, R. P., "Coal-Derived Asphaltene: Effect of Phenol Content and Molecular Weight on Viscosity of Solutions", Fuel, 59, 621-626 (1980).
- (5) Brown, F. R. and Karn, F. S., "Stability Studies of Coal Liquids", PETC/TR-79/5.
- (6) Oswald, G. E., Youngblood, E. L., and Hightower, J. R., Jr., "Rheological Characterization of Coal-Solvent Slurry at High Temperature and Pressure", AIChE Meeting, Philadelphia, Pennsylvania, June 8-12, 1980.

REFERENCES
(Continued)

- (7) Droege, J. W., Hassell, J. A., and Chauhan, S. P., "Viscosity at Elevated Temperature and Pressure of Coal-Derived Liquids", Proc. 7th Symp. Thermophysical Prop., Gaithersburg, Maryland, May 10-12, 1977, ASME.
- (8) Smith, T. L., Ferry, J. D., and Schremp, F. W., J. Appl. Phys., 20, 144-153 (1949).



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