APPENDIX D

VISCOSITY AND DENSITY OF H-COAL PDU LIQUID SLURRY SAMPLES: OAK RIDGE NATIONAL LABORATORIES FINAL REPORT

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
UNION CARBIDE CORPORATION
NUCLEAR DIVISION

POST OFFICE BOX X
OAK RIDGE, TENNESSEE 37830

July 8, 1981

Mr. Robert J. Schaefer
Amoco Oil Company, H-6
P. O. Box 400
Naperville, Illinois 60566

Dear Bob:

Enclosed is our final report on viscosity and density measurements of the H-Coal samples. This will be published soon.

If you have any questions, do not hesitate to call.

Sincerely,

Bob Hightower

J. R. Hightower, Jr., Head
Advanced Technology Section
Chemical Technology Division

JRH:jts

Enclosure

cc: D. D. Lee
B. R. Rodgers
J. H. Wilson

ORNL/TM-7915

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CHEMICAL TECHNOLOGY DIVISION

FINAL REPORT - H-COAL PRODUCT PHYSICAL PROPERTIES MEASUREMENT

D. D. Lee

Date Published:

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

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FINAL REPORT - H-COAL PRODUCT PHYSICAL PROPERTIES MEASUREMENT

D. D. Lee

ABSTRACT

Rheological and density measurements have been made on the H-Coal PDU reactor effluent samples from run PDU-10, periods 27B, 34A, 42A, and 43A, which used Wyodak coal. The characterization was done in the ORNL Coal Liquids Flow System (CLFS) at 719 K and 19.3 MPa, which closely approximated the conditions in the H-Coal PDU reactor at the time the samples were taken. Under these conditions, the apparent viscosities of the samples at a shear rate of 300 s^{-1} were 2.1, 4.0, 2.5, and 1.5 mPa·s (cP), respectively. The corresponding densities were 0.908, 0.985, 0.882, and 0.851 g/cm^3. The rheological data were fitted to both power law and Bingham plastic models. Samples 27B and 34A were described almost equally well by both models, while samples 42A and 43A were better described by the Bingham plastic model. The apparent viscosities appeared to correlate to the amount of solids in the samples.

1. INTRODUCTION

The density and rheology of H-Coal PDU reactor effluent collected in high-pressure sample bombs during PDU operation have been measured at the temperatures and pressures of reactor operation. Such information is needed for the design and operation of the ebullated-bed reactor. The viscosity determines the minimum liquid recirculation rate necessary for fluidization of the catalyst bed, and the maximum rate above which catalyst particles

are carried out of the reactor. The samples 27B, 34A, 42A, and 43A were taken during PDU run No. PDU-10. The sample information is shown in Table 1. The measurements were made in the ORNL Coal Liquids Flow System (CLFS), which is designed to operate at up to 810 K and 31 MPa. The CLFS consists of a slurry feed system (1.2 g/s capacity), slurry preheater, reactor, high-pressure hydrogen or inert gas supply, vapor-liquid separator, and liquid and gas pressure letdown systems. The liquid stream from the preheater exit is passed through the physical property instruments at the desired process conditions for measurement.

Table 1. Data for H-Coal PDU effluent samples

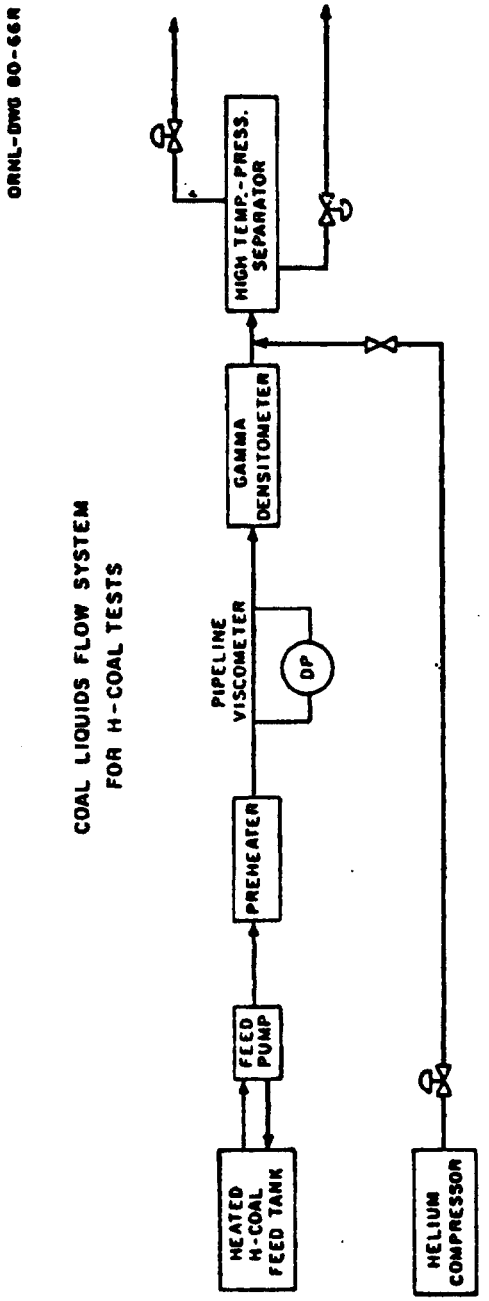
Data Component	Sample 27B	Sample 34A	Sample 42A	Sample 43A
PDU run No.	PDU-10	PDU-10	PDU-10	PDU-10
PDU period No.	27B	34A	42A	43A
Feed rates				
Coal, kg/h	111	106	107	105
Liquid, kg/h	179	186	207	207
Gas, m^3/h	203	207	209	272
Liquid/coal weight ratio	1.61	1.75	1.92	1.96
Coal type	Wyodak	Wyodak	Wyodak	Wyodak
Reactor temperature, K	719	719	716	718
Reactor pressure, MPa	19.3	19.6	19.3	19.3

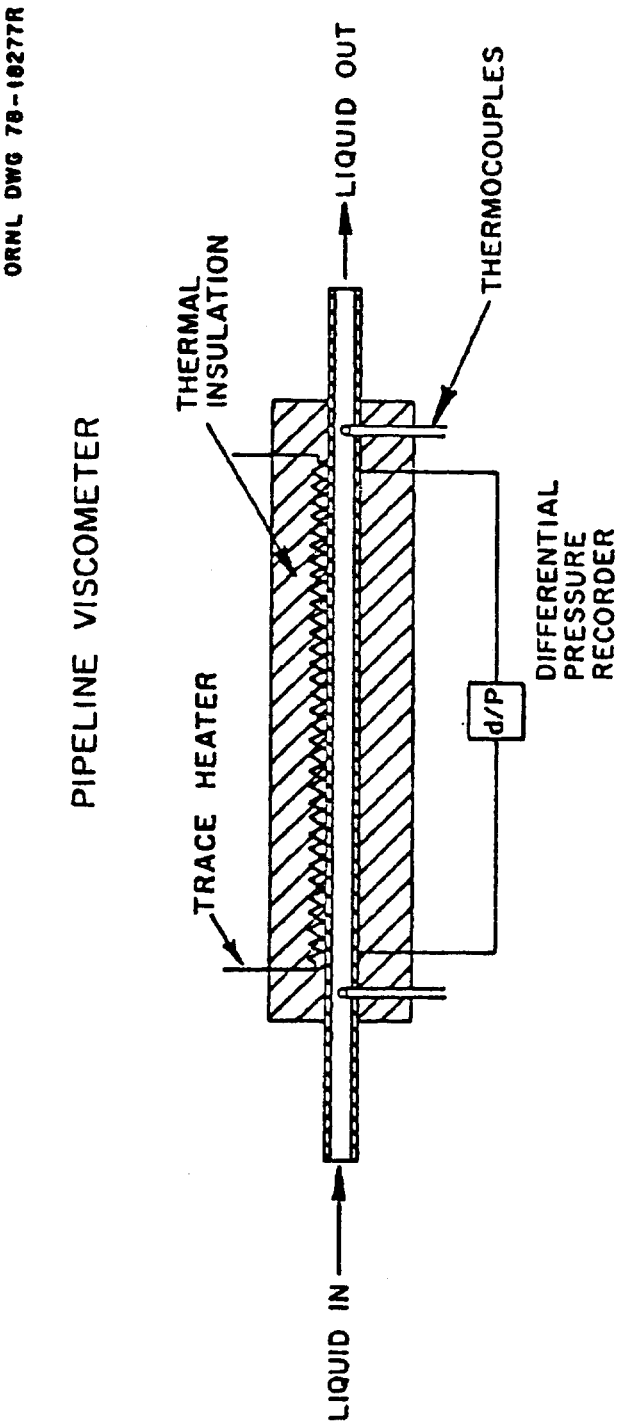
2. EXPERIMENTAL APPARATUS

The Coal Liquids Flow System (CLFS), shown schematically in Fig. 1, was designed to permit study of both rheological properties and density of coal liquefaction process streams. For measurement of H-Coal samples, the basic CLFS was modified by adding heating tapes and insulation to the outside of the feed tank and fitting the tank for operation under slight helium pressure (<100 kPa). The H-Coal slurry was heated to 400 K in the feed tank to permit easy flow to the measurement system. A Bran-Lubbe positive displacement pump was used to feed the sample to the preheater, which is a 12-m-long serpentine coil of 2.8-mm-ID stainless steel tubing wrapped with high-temperature electrical resistance heating tape capable of supplying 2.2×10^4 J/s·m^2 heat flux. The pipeline viscometer (PLV) (0.61 m long) of the same internal diameter as the preheater is located immediately downstream from the preheater. Figure 2 is a schematic diagram of the viscometer. The viscometer is equipped with a differential pressure cell for measuring the pressure drop across the viscometer and two chromel-alumel thermocouples for measuring the inlet and outlet slurry temperatures.

Located downstream of the viscometer is the gamma-radiation absorption instrument, which is used for measuring the density of coal liquids and slurries. Figure 3 is a schematic of the experimental assembly, which consists of the commercially available gamma-radiation absorption instrument* and a 0.030-m-ID x 0.042-m-OD pressure vessel, which was constructed at ORNL. Density is determined by the attenuation of 662-keV gamma rays from the ^{137}Cs source as they pass through the fluids. The attenuation by

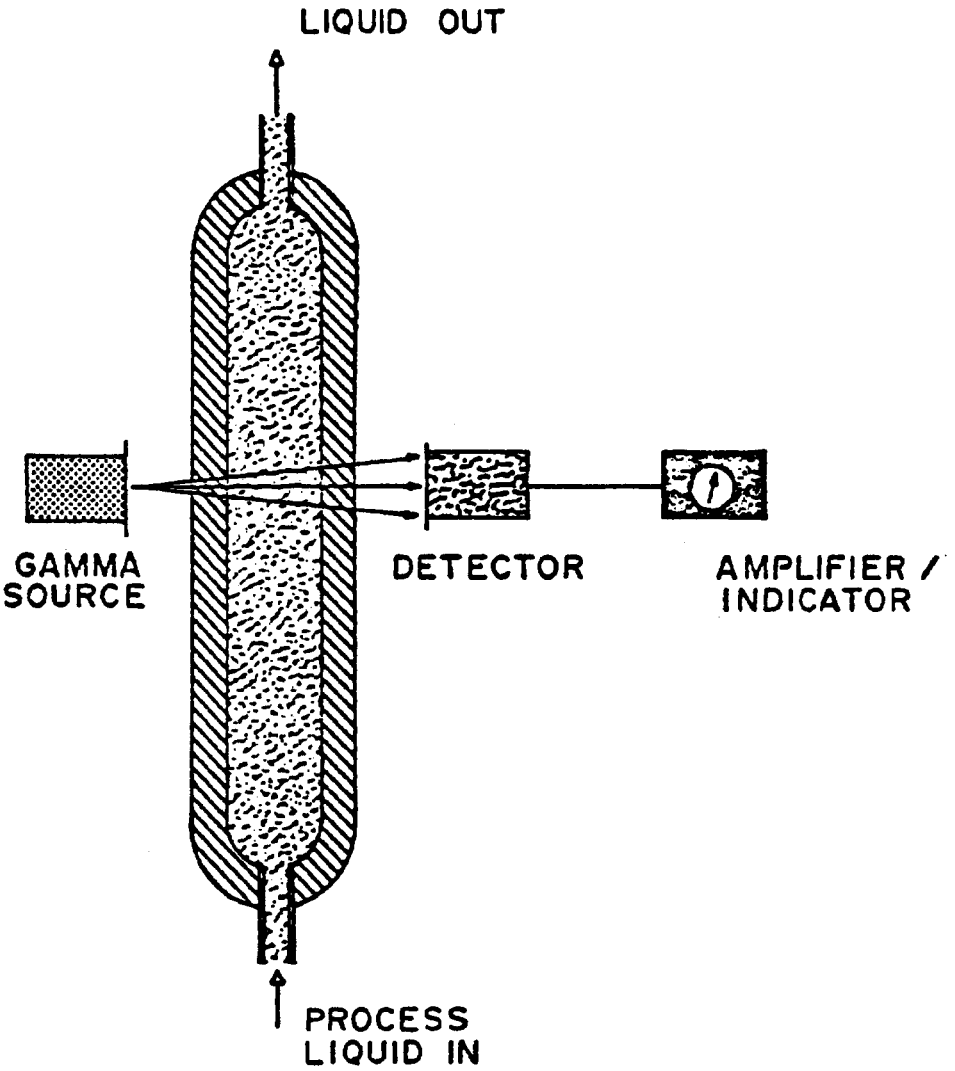
*Kay-Ray 3600F Liquid-Slurry Density System manufactured by Kay-Ray, Inc., 516 W. Campus Dr., Arlington Heights, Ill.


ORNL-DWG 80-668
COAL LIQUIDS FLOW SYSTEM
FOR H-COAL TESTS
HEATED H-COAL FEED TANK
FEED PUMP
PREHEATER
PIPELINE VISCOMETER
DP
GAMMA DENSITOMETER
HIGH TEMP.-PRESS. SEPARATOR
HELIUM COMPRESSOR


ORNL DWG 78-10277R
PIPELINE VISCOMETER
LIQUID OUT
THERMOCOUPLES
THERMAL INSULATION
DIFFERENTIAL PRESSURE RECORDER
d/P
TRACE HEATER
LIQUID IN

ORNL DWG. 78-1128

GAMMA ABSORPTION LIQUID DENSITY GAUGE



the pressure vessel and the correction for the pressure vessel expansion with temperature are taken into account.

3. EXPERIMENTAL PROCEDURE

In preparation for the rheological characterization and density measurements, the slurry was removed from each of the sample bombs in turn (7-liter capacity each) by first melting the slurry by heating the surface of the bomb to ~435 K. The slurry was discharged from the bombs directly into the feed tank by applying helium overpressure. About 3 to 5 kg of material was recovered from each bomb. The material was placed in a stirred and heated feed tank. The slurry mass feed rate to the system was determined by continuously monitoring the feed tank weight with an electronic load cell. Feed tank temperature was controlled at 400 K. The slurry displayed almost no tendency to settle out. Therefore, the feed to the Bran-Lubbe pump was maintained by a slight positive gas pressure (<5 psig) on the feed tank rather than by a recirculating pump as in normal operations. The feed pump and the lines were heat traced and controlled at 400-450 K to maintain fluidity. Samples 27B and 43A were easily deformable at room temperature, while 34A and 42A were slightly firmer. The preheater was operated with constant heat flux along its length; heat input was controlled such that the slurry just reached the measurement temperature at the preheater exit–viscometer entrance. Thus, slurry residence time at the measurement temperature before it entered the viscometer was zero. The viscometer was maintained at the measurement temperature by an independent trace heat system.

The slurry then passed into the gamma-radiation absorption density instrument at the viscometer discharge. The density measurements were made at the same time as the rheology tests. The slurry feed rate was varied and density was measured at each feed rate for samples 27B, 34A, and 42A and measured at the first rate for sample 43A. The slurry was kept at the measurement temperature by trace heating on the density instrument feed lines and by a separate control circuit on the pressure vessel wall, which was maintained at 719 K. The output voltage of the density instrument was recorded by the on-line digital computation system. The gamma-density instrument calibration was checked before and after each run and calibrated as described previously.[1] For the first two samples, the H-Coal slurry from the CLFS was collected in high-pressure sample bombs so it could be reused if needed. However, a line between the bomb and the off-gas letdown valve plugged on the run with the third sample, and the slurry was diverted to the regular product tank. The slurry was also caught in the regular product tank in the fourth sample run because of solvent purging of the dp cell lines on the PLV, which diluted the H-Coal.

The viscometer differential pressure, inlet and outlet temperatures, and the slurry mass flow rate (varied from 0.1 g/s to 1.4 g/s) were recorded by the on-line digital computer data acquisition and analysis system. Each sample run lasted about 1-1/2 h while data were being taken, and the total time including heatup, cool-down, and calibration lasted about 10 h. Data are shown in Tables 2 and 3. There was no evidence of additional slurry liquefaction reactions as the data were being taken.

Table 2. Results of CLFS runs on H-Coal PDU-10: samples 27B, 34A, and 42A

Sample	Feed rate (g/s)	Average PI.V ΔP (kPa)	Average PI.V temperature (K)	Densitometer temperature (K)	Density (g/cm^3)	$8V/D$ (s^{-1})	τ_w (N/m^2)	Apparent viscosity $\tau_w/\dot{\gamma}_w$ (mPa·s)
27B	1.162	1.00	715	728	0.931	595	1.132	1.76
	1.128	1.00	711	728	0.937	575	1.132	1.77
	0.689	0.70	718	729	0.921	353	0.792	2.03
	0.750	0.75	717	728	0.921	384	0.849	1.98
	0.469	0.52	712	727	0.907	239	0.594	2.26
	0.232	0.35	706	729	0.897	118	0.396	2.75
	0.155	0.22	697	724	0.872	78	0.255	3.08
	0.340	0.37	701	722	0.876	172	0.424	2.48
34A	0.449	0.92	706	720	0.981	217	1.047	4.38
	0.441	0.90	710	734	0.952	214	1.019	4.41
	0.832	1.40	721	727	0.987	405	1.585	3.78
	0.827	1.42	721	718	0.987	402	1.613	3.72
	1.048	1.72	719	717	1.002	509	1.952	3.50
	1.025	1.72	721	717	0.994	499	1.952	3.52
	0.658	1.24	721	720	1.001	320	1.415	3.96
	0.710	1.27	721	722	0.980	345	1.443	3.88
	0.686	1.27	722	724	0.980	334	1.443	3.81
	0.266	0.75	714	716	0.986	129	0.849	5.04
42A	0.650	0.87	710	718	0.899	348	0.990	2.61
	1.324	1.40	721	723	0.882	716	1.585	2.03
	0.921	1.15	719	720	0.894	497	1.302	2.40
	1.217	1.20	710	718	0.876	652	1.358	1.91
	0.523	0.67	705	718	0.891	279	0.764	2.51
	0.702	0.77	710	721	0.872	376	0.877	2.14
	0.405	0.77	709	720	0.874	217	0.877	3.71
	0.251	0.72	705	720	0.874	134	0.821	5.63
	0.158	0.55	697	722	0.874	84	0.622	6.82

Table 3. Results of CLFS run on H-Coal PDU-10, sample 43A, reactor effluent slurry

Time	Feed rate (g/s)	PLV ΔP (kPa)	Avg PLV (K)	Density[a] (g/cm^3)	$8V/D$ (s^{-1})	τ_w (N/m^2)	$n = \left(\frac{d \ln \tau_w}{d \ln 8V/D}\right)$	$\dot{S}_w = \left(\frac{8V}{D} \cdot \frac{3n+1}{4n}\right)$	$\tau_w = k\dot{S}_w^n$ (N/m^2)	Apparent viscosity $\tau_w/\dot{S}_w$ (mPa·s)
1238	0.665	0.750	716	0.851	374	0.608	0.838	392	0.612	1.56
1304[b]	0.880	0.949	711		493	0.770	0.838	517	0.771	1.49
1312	1.377	1.395	716		785	1.132	0.838	823	1.138	1.38
1324[b]	0.450	0.617	696		249	0.501	0.473	318	0.501	1.58
1332	0.329	0.562	699		183	0.456	0.244	324	0.461	1.42
1342[b]	0.174	0.488	691		96	0.396	0.244	170	0.394	2.32
1349	0.109	0.433	692		60	0.351	0.244	106	0.351	3.30
1403[b]	1.025[c]	0.102	708		574	0.894	0.838	602	0.876	1.45
1411	0.665[c]	0.757	710		373	0.614	0.838	391	0.610	1.56

[a]Density was measured only during the first data point.

[b]Pipeline viscometer pressure taps purged before measurement.

[c]Corrected readings from weigh cell recalibration tests.

4. DATA ANALYSIS AND DISCUSSION

To produce a rheogram from the viscometer differential pressure vs flow rate data at constant temperature, the Rabinowitsch-Mooney (R-M) analysis was used. For steady, time-independent laminar flow, a log-log plot of the R-M parameter, $8V/D$, vs the wall shear stress is made. Flow rate measurements were used to determine the slurry superficial velocity (V), and the viscometer internal diameter (D) was precisely measured. The wall shear stress (τ_w) is determined from a force balance over the length (L) of the viscometer,

$$\tau_w = \frac{D\Delta P}{4L}, \tag{1}$$

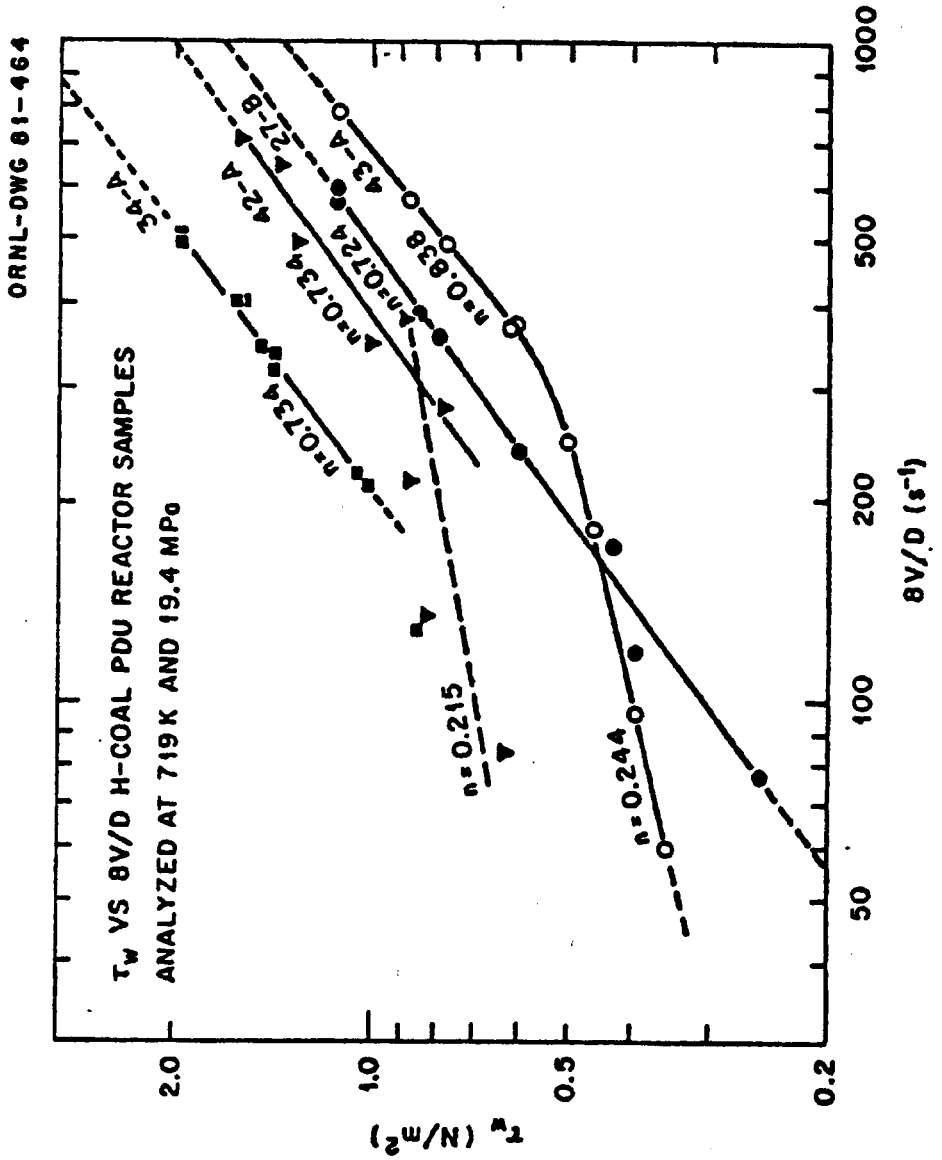
where ΔP is the pressure drop across the viscometer. Figure 4 shows the flow curves developed for the H-Coal samples.

To construct a rheogram, values of wall shear rate are determined over the range of wall shear stress achieved during each series of measurements at constant temperature and pressure. This is accomplished by determining the slope (n) of the flow curve at various values of wall shear stress (τ_w). The slopes are then used in the Rabinowitsch-Mooney relation to convert the corresponding $8V/D$ value to the wall shear rate ($\dot{S}_w$):

$$\dot{S}_w = 8V/D \left(\frac{3n + 1}{4n}\right). \tag{2}$$

If the power law model is assumed (linear behavior of the flow curve) to describe the flow behavior,

$$\tau_w = k\dot{S}^n_w, \tag{3}$$


ORNL-DWG 81-464
τ_w VS 8V/D H-COAL PDU REACTOR SAMPLES
ANALYZED AT 719 K AND 19.4 MPa
n=0.838
n=0.724
n=0.734
n=0.734
n=0.215
n=0.244
43-A
42-A
42-B
τ_w (N/m^2)
8V/D (s^{-1})
2.0
1.0
0.5
0.2
50
100
200
500
1000

where k is the consistency factor determined from the flow curve by

$$k = \tau_w \left(\frac{3n + 1}{4n}\right)^{-n} \tag{4}$$

at $8V/D = 1$ and n is called the flow behavior index. The slurry is Newtonian if n is equal to 1, pseudoplastic if the slope is less than 1, and dilatant if the slope is greater than 1.

The data can also be fitted to the Bingham plastic model using the analytical solution for the Rabinowitsch-Mooney analysis assuming Bingham plastic behavior.[2] Thus,

$$8V/D = \frac{\tau_w}{\eta} - \frac{\tau_y^4}{3\eta} + \frac{\tau_y^4}{3\eta\tau_w^3} \quad , \tag{5}$$

where τ_y is yield stress and η is plastic viscosity in the Bingham plastic constitutive equation

$$\tau_w = \tau_y + \eta\dot{S}_w \, . \tag{6}$$

The plots on rectangular coordinates of τ_w vs $8V/D$ for the H-Coal samples are shown in Fig. 5.

The results of the rheological analyses are presented in Table 4, and the chemical analyses of the samples are shown in Table 5. From Table 4 and Figure 5, the data for all of the H-Coal samples fit the Bingham plastic model quite well. From Table 4 and Figure 4, the data for samples 27B and 34A also fit the power law model. However, using the power law model, the data for samples 42A and 43A produced two different slopes for each sample which depended on the shear rate. Below $8V/D = 300\ s^{-1}$, the slopes are

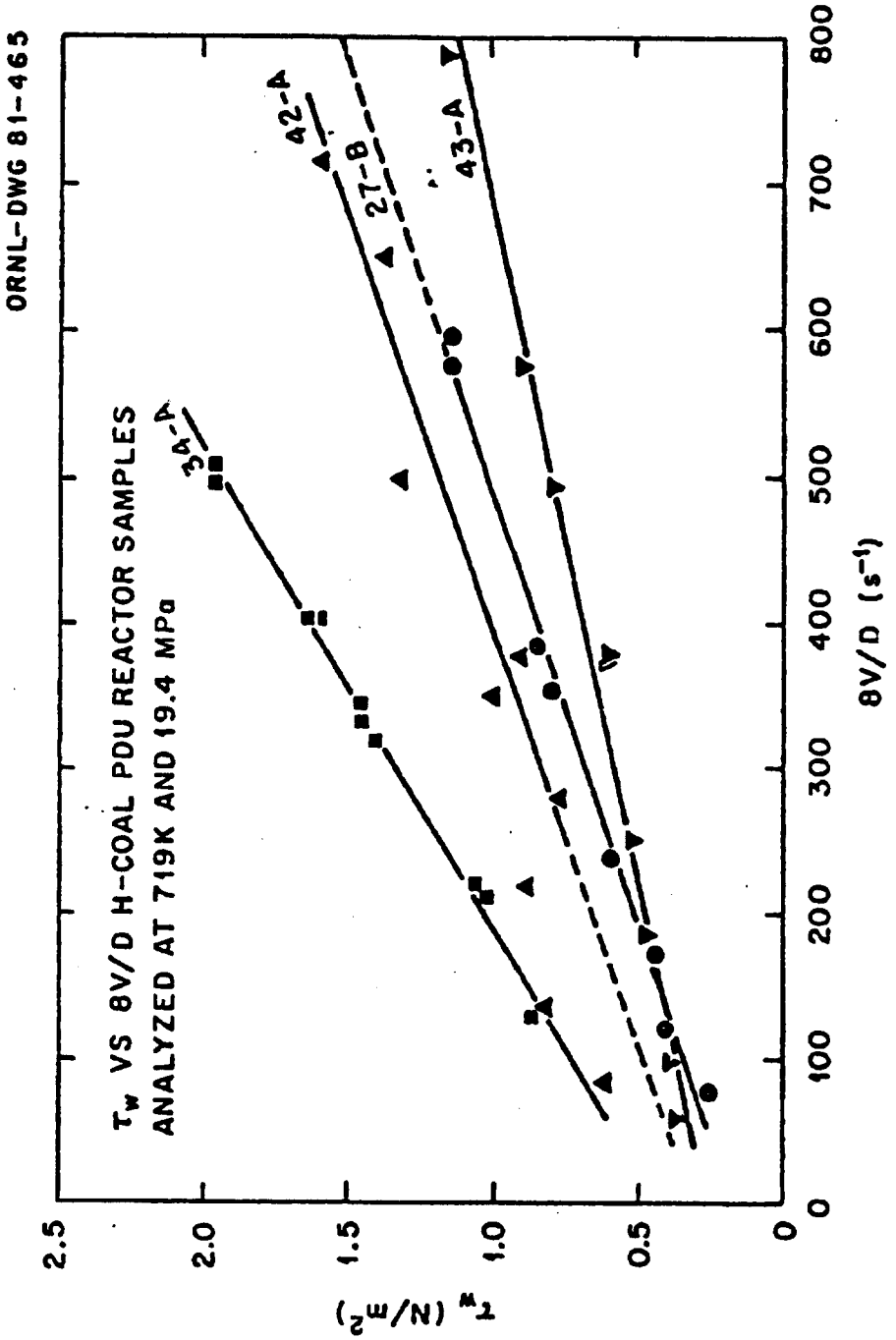

ORNL-DWG 81-465
τ_w VS 8V/D H-COAL PDU REACTOR SAMPLES
ANALYZED AT 719K AND 19.4 MPa
34-A
42-A
27-B
43-A
τ_w (N/m^2)
8V/D (s^{-1})
0
0.5
1.0
1.5
2.0
2.5
100
200
300
400
500
600
700
800

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Table 4. Rheological analyses results[a]

Sample No.	Power law model parameters				Bingham plastic model				Density (g/cm^3)
	Slope	k	r^2	μ_a	τ_y	η	r^2	μ_a	
PDU-10-27B	0.724	10.51	0.989	2.18	127.0	1.68	0.990	2.10	0.908
PDU-10-34A	0.724	18.80	0.993	4.12	306.7	3.03	0.993	4.05	0.985
PDU-10-42A	0.734[b]	11.75	0.927	2.58	232.4[c]	1.73	0.919	2.51	0.882
PDU-10-42A	0.215[d]	225.3	0.632	2.56					
PDU-10-43A	0.838[e]	4.11	0.998	1.63	191.1[c]	1.07	0.983	1.71	0.838
PDU-10-43A	0.244[f]	112.3	0.997	1.51					

[a] k = consistency factor ($mN \cdot s^n/m^2$).

r^2 = correlation coefficient for least squares analysis.

μ_a = apparent viscosity at $\dot{S} = 300\ s^{-1}$ ($mPa \cdot s$).

τ_y = yield stress (mN/m^2).

η = plastic viscosity ($mN \cdot s/m^2$).

[b] Calculations based on $8V/D > 200\ s^{-1}$.

[c] Calculations based on $8V/D = 50$ to $800\ s^{-1}$.

[d] Calculations based on $8V/D < 400\ s^{-1}$.

[e] Calculations based on $8V/D > 300\ s^{-1}$.

[f] Calculations based on $8V/D < 300\ s^{-1}$.

Table 5. Chemical analysis of H-Coal PDU samples

Component	Sample 27B (wt %)	Sample 34A (wt %)	Sample 42A (wt %)	Sample 43A (wt %)
Carbon	77.9	78.7	78.4	80.3
Hydrogen	6.3	6.2	6.7	7.2
Nitrogen	0.7	0.8	0.8	0.7
Sulfur	0.3	0.4	0.5	0.4
Oxygen (by difference)	2.5	1.4	1.5	1.6
Ash	12.3	12.5	12.1	9.8
Density at 294 K, g/cm^3	1.204	1.238	1.201	1.171
Soxhlet extraction				
Pentane sol and benzene sol (oils)	54.5	52.9	59.4	67.8
Pentane insol and benzene sol (asphaltenes)	4.5	8.6	7.2	9.0
Pyridine sol and benzene insol (preasphaltenes)	4.9	5.6	4.7	0.7
Pyridine insol and benzene insol (residue)	36.1	32.9	28.7	22.5

very low ($\sim$0.2), while above that value the slopes are comparable to or higher than those of 27B and 34A. However, there is some question about the data below $8V/D = 300\ s^{-1}$ for 42A because of possible viscometer pressure tap plugging.

As the reaction conditions under which the four H-Coal samples were produced were very similar, the same rheological behavior would be expected.

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From Fig. 4, samples 27B and 34A have points at the lower shear rates, which could indicate a change in slope of the power law model. Sample 34A, for example, has a data point at approximately 130 s^{-1}, which lies significantly above the line with the 0.734 slope. Also from Fig. 4, if the data point at 78 s^{-1} were eliminated, sample 27B appears to exhibit a change in slope at the lower shear rates. Additional data would be desirable in order to determine if samples 27B and 34A actually do behave like samples 42A and 34A in the low shear-rate region.

As seen in Table 1, the liquid/coal weight ratio was the only processing parameter that showed significant variation for the four H-Coal samples. The gas feed rate was relatively high for sample 43A, but was essentially the same for the other three samples. There appears to be no correlation of the viscosity of the samples with the given processing conditions.

From Table 4, the chemical analyses demonstrated variations between the H-Coal samples primarily in density and the Soxhlet extraction results. The ash level of sample 43A was lower than that of the other three samples. The elemental compositions of all samples were very similar. Using the results from Table 4, there does appear to be a correlation between the apparent viscosity and density; i.e., the higher the density, the higher the viscosity. As density should be related to the amount of solids (ash plus unconverted coal) in the samples, such a correlation would appear reasonable. However, as pyridine insolubles should also be a measure of solids, the apparent viscosity would also be expected to correlate with this parameter, which does not seem to be the case. If, though, the pyridine insolubles result from sample 27B was in error and

was actually close to that of sample 42A, then a correlation would exist. It is quite conceivable that this analytical result for sample 27B could be high, as indicated by the ash level, which should also be a measure of solids. Even though there is not much variation in each level between samples 27B, 34A, and 42A, the apparent viscosities do appear to increase with increasing ash level.

5. REFERENCES

1. *Fossil Energy Program Quarterly Progress Report for the Period Ending September 30, 1979,* ORNL-5612 (January 1980).

2. A. H. P. Skelland, *Non-Newtonian Flow and Heat Transfer,* Wiley, New York, 1967, pp. 28-38.