

THE EFFECTS OF SUSPENDED RESIDUAL SOLIDS ON THE RHEOLOGY OF COAL-DERIVED LIQUIDS

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ABSTRACT

The rheology of the products of coal liquefaction was investigated using a Weissenberg Rheogoniometer, Model R-16, modified to allow total-normal-force measurements. Solvent extracted oils and asphaltene fractions were tested separately and when in combination with the preasphaltene fraction and residual solids. The solids-free fractions showed slight shear thinning and very little viscoelasticity. Solids-free liquids containing asphaltenes showed positive first-normal-stress differences and negative second-normal-stress differences, both varying with approximately the first power of shear rate. The addition of residual solids to the coal-derived liquids caused a dramatic change in rheology for H-Coal liquefaction material. Pronounced shear thinning was observed for solids concentrations greater than 15 wt.% in a mixture of H-Coal oils, asphaltenes and preasphaltenes. Time-temperature superposition of viscosity isotherms indicated finite zero-shear viscosities. The addition of solids enhanced the viscoelasticity, giving dynamic rigidities which increased weakly with increasing frequency. The presence of suspended residual solids also altered the shear rate dependence of the normal stress differences. The first-normal-stress difference was positive and varied with approximately the second power of shear rate. The second-normal-stress difference was negative, varying with approximately the 0.7 power of shear rate.

The effects of shear rate history on the transient behavior at the onset of steady shearing support the conclusion that residual solids in coal-derived liquids can form loose flocs. It is further concluded that these flocs immobilize significant amounts of liquid giving large zero-shear viscosities. The floc network imparts an elastic character to the coal-derived material and the breakdown of this floc with increasing shear rate gives the observed shear thinning.

INTRODUCTION

The "liquid" products of coal liquefaction include oils, asphaltenes, preasphaltenes and residual solids [1]. The residual solids are composed of undissolved portions of the coal, primarily mineral matter and char which is generated during liquefaction. The residual solids are finely dispersed in the

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coal-derived liquids with particle size distributions extending into the sub-micron range. Stringent federal standards for combustible fuels and the need for low-ash feedstocks for catalytic upgrading demand the removal of most of these dispersed solids. The elimination of such solids is not easily done and has been identified as one of the critical problem areas in coal liquefaction [2].

Chemical analyses have shown the content of sulfur, nitrogen and oxygen (i.e., the heteroatom content) to increase when going from the oils to preasphaltenes fraction [3, 4, 5]. Also, the percent aromatic carbon and aromatic hydrogen contents [4, 5] and molecular weights [3, 4, 5, 6] have been observed to increase when going from oils to preasphaltenes.

Since hydrogen bonding increases with heteroatom content and charge-transfer complexing increases with aromatic content, one would expect the asphaltene and preasphaltene fractions to be more associated and to exhibit higher viscosities than the coal-derived oils. Viscosity testing of coal-derived liquids has shown this to be the case. Sternberg et al. [7] found the preasphaltene fraction to have the most pronounced effect on the viscosity of Synthoil products. Thomas and Granoff [8] derived an empirical correlation for the viscosity of hydroliquefaction products as a function of preasphaltene and asphaltene content. This correlation shows preasphaltenes to have the dominant effect on viscosity. Other investigators, looking more closely at the effect of chemical functionality on viscosity, have found that hydrogen bonding between phenolic hydrogen and basic nitrogen acts to significantly increase the viscosity of coal-derived liquids [9, 10].

Methods of solids separation under development for use in coal liquefaction include mechanical filtration, hydrocloning, centrifuging, settling, electrostatic precipitation and magnetic separation. These methods involve the movement of residual solids relative to the heavier coal-derived liquids. A knowledge of the rheology of the heavier coal-derived liquids and of the colloidal behavior of the dispersed solids would lead to a better understanding of solids separation. Accordingly, this research was directed to studying the rheology of coal-liquefaction products with and without suspended solids. Observation of the effects of solids on rheological behavior can give insight to the colloidal state of a dispersed system.

The rheological properties measured in this work were the complex viscosity and the viscometric functions. The viscometric functions are comprised of the apparent viscosity, and the first and second-normal-stress differences. Although these rheological properties are not sufficient to describe the rheology of general flows or even elementary flows of general fluids, their measurement represents a substantial step up from the usual rheological characterization of coal-derived liquids, i.e., viscosity measurements. Moreover, for suspensions in general, little has been done with regards to measuring the normal stress differences [11]. Such information could serve as a test of existing constitutive theory as well as giving more insight to the physical state of a suspension during flow.

MATERIALS AND METHODS

Preparation of materials

Two types of coal liquefaction products were utilized in this study. The bulk of the experimental testing was done using vacuum-still bottoms from the H-Coal process of Hydrocarbon Research, Inc. The other material tested was SRC product generated by the Solvent Refined Coal process at Wilsonville, Alabama.

Both types of material were batch extracted using a series of solvents with increasing polar strengths. 1.13 kg quantities of liquefaction material were extracted in a 12 l extraction vessel using approximately 4.5 l of solvent. First, the coal-derived material was extracted with *n*-pentane. The vessel was heated using a heating mantle and the mixture was stirred using a whip-like stirring rod driven by an electric motor. Solvent vapors were condensed and returned to the vessel using a reflux condenser. Oxygen was purged from the vessel before heating using nitrogen. Following the extraction, the slurry was filtered through a Buchner funnel. The filter cake was then placed back into the extraction vessel and extracted in an analogous manner using toluene. The insolubles from the toluene extraction were next extracted using tetrahydrofuran.

The H-Coal oils were recovered from the pentane by distilling off the bulk of the solvent and then air drying at room temperature until there was no more pentane odor. The H-Coal asphaltenes and preasphaltenes were recovered by distilling off the bulk of their solvents, air drying for a prescribed time, and then vacuum drying. The asphaltenes were air dried at room temperature for two weeks and then vacuum dried at 105°C for four hours. The preasphaltenes were air dried for one week at room temperature and then vacuum dried at 55°C for four hours. No solvent odors were detected after drying. Some oxidation may have occurred during the air drying stage, but it is thought that at room temperature and under unstirred conditions it would not be severe. Some support for this was given by Karn [12] in his viscosity experiments on Synthoil product. Also, elemental analyses of these H-Coal fractions did not show abnormally high percentages of oxygen. In this study it was found that when the H-Coal fractions were recombined in the same weight ratios as those occurring in the unextracted H-Coal material, the viscosity behavior of the recombined sample was qualitatively similar to that of the unextracted material. Quantitative agreement was never off by more than a factor of two. This difference is most likely the result of volatiles lost during vacuum drying and perhaps some oxidation. Qualitative rheological trends were the object of this research since the rheology of a coal-derived liquid can be expected to vary depending not only on the liquefaction processing conditions but also on the source coal. In the case of the lower-boiling SRC product, fractions were recovered by distilling off all of the solvent. No air drying or vacuum drying was involved.

Corresponding fractions from each extraction series were combined to provide uniform samples of oils, asphaltenes, and preasphaltenes. These samples were stored in glass jars in a freezer to reduce aging effects. Indeed, no significant quantitative changes in viscosity were observed over the period of this research.

In addition to rheological testing of individual fractions, mixtures of fractions were tested to assess compositional effects. Mixtures of fractions were made by dissolving the required amounts of each fraction in tetrahydrofuran and then stripping off the tetrahydrofuran in a vacuum oven. Preparation of samples with varying solids contents (tetrahydrofuran insolubles) was more difficult since mixing the solids directly into the coal-derived liquids resulted in nonhomogeneous suspensions. It was found that homogeneous suspensions could be attained using the unextracted liquefaction product, the H-Coal vacuum-still bottoms in this case. The unextracted H-Coal material, with a solids content of 31.2 wt.%, was dissolved in tetrahydrofuran and the amounts of oils, asphaltenes, and preasphaltenes necessary to lower the solids content to the desired level were added. The tetrahydrofuran was then removed by drying in a vacuum oven. Tests on a sample of H-Coal material which had been dissolved in tetrahydrofuran and then dried, showed no substantial change in viscosity when compared with the untreated H-Coal material. This method allowed the preparation of samples with solids contents varying from 31.2 wt.% to 0 wt.%. A constant weight ratio of oils, asphaltenes, and preasphaltenes was maintained for all solids concentrations to better evaluate the effect of the solids.

Apparatus for rheological testing

Rheological testing was done using a Weissenberg Rheogoniometer, Model R-16. This instrument is capable of performing steady-shear and oscillatory testing. It also has a normal force option but it is costly and can be troublesome. For this work a modification was made to the rheogoniometer to allow total-normal-force measurements as is shown in Fig.1. A piezoelectric force transducer was mounted between the platen and the platen holder on the upper torsion shaft. This was a type 902A quartz load washer manufactured by Kistler Instruments Corporation. This transducer was sandwiched between two stainless steel mounts which were specially constructed to provide flush surfaces for uniform load distribution on the transducer. The two mounts were connected by a central post on the lower mount which extended through the hole in the load washer and screwed into the upper mount. The central post of the mount was made thin (0.357 cm in diameter) to allow most of the load to be carried by the transducer and to thus maintain transducer sensitivity. A change in total-normal-force on the upper platen causes the generation of an electrostatic charge in the quartz crystal of the transducer which is converted to voltage through a charge amplifier. Calibration of the transducer showed a sensitivity of about 493 dyne/mv

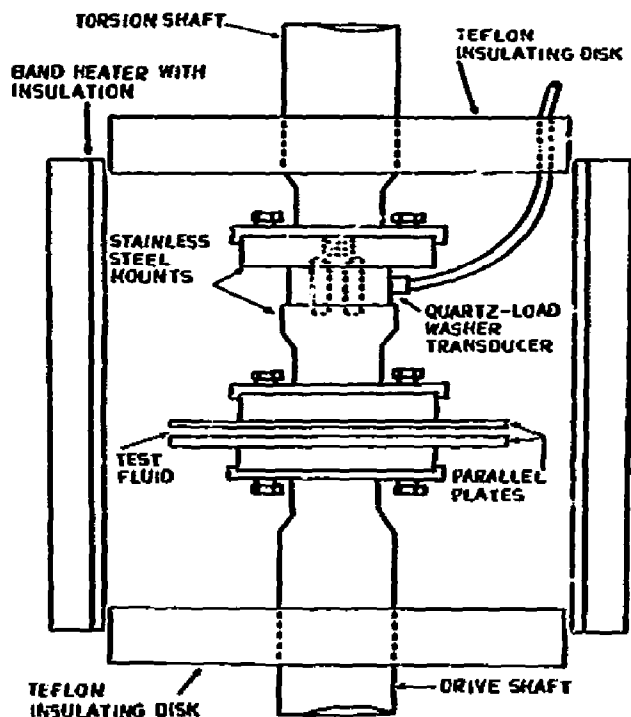


Fig.1. Modification of the Weissenberg Rheogoniometer, Model R-16, to accommodate a quartz load washer transducer for making total normal force measurements; also shown is the specially designed heating oven.

and a pressure sensitivity of about 45 dynes/cm^2 when averaged over a 7.5 cm diameter platen. The load washer was sensitive to both compression and tension. The performance of this system of total normal force measurement was tested by shearing a Newtonian fluid over shear rates varying from 100 to 1000 s^{-1} . The transducer indicated tensile forces with magnitudes very close to those which would be expected due to primary inertial effects. Additional details concerning this system have been published elsewhere [13].

Parallel-plate and cone-and-plate platens were used for all testing. The platens were heated to the desired temperature using a specially designed heating system. An 11.43 cm ID 750 W band heater was attached to a sliding mount on the support column of the rheogoniometer. The top and bottom of the oven consisted of Teflon disks which were clamped to the upper torsion shaft and the lower drive shaft. Small gaps were left between the Teflon disks and the heater wall to permit free movement. The temperature in the oven was controlled using a proportional-integral controller. This heating system provided fast heating rates, convenience in sample loading, and good temperature control.

Since tetrahydrofuran was used to clean the platens, an exhaust hood was built over the rheogoniometer. This also served to vent off any carcinogenic vapors coming from the coal-derived liquids.

Rheological calculations

Equations giving the viscosity for steady-shear testing using parallel-plate and cone-and-plate geometries have been well stated by Schowalter [14]. Viscosity calculations for the parallel plate geometry are more cumbersome than those for the cone-and-plate geometry. However, parallel plates have the advantage of having a variable gap between platens which expedites sample loading.

Equations for calculating the normal stress differences from total-normal-force data have been presented by Walters [15]. The first-normal-stress difference can be directly calculated from total-normal-force data when taken using the cone-and-plate geometry. Calculation of the second-normal-stress difference requires duplicate testing using two platen geometries. In this work, parallel plate data were used along with cone-and-plate data for higher shear rates. For lower shear rates, the extended cone-and-plate geometry as described by Schowalter [14] was used in place of cone-and-plate testing in order to reduce cyclical fluctuations which were more severe at smaller platen separations. Since testing at higher shear rates was required in this work, it was necessary to correct for inertial effects. The correction to the total normal force accounting for inertial pressures generated by the primary flow (F_c) is given by Walters [15] as:

$$F_c = -3\pi\rho\Omega^2R^4/40 \quad (1)$$

where ρ is the fluid density, Ω is the angular velocity and R is the platen radius. This correction was used for all testing geometries.

Oscillation testing was done using the parallel plate geometry since fluid inertia was accounted for in the equations of motion. The solution for the velocity field between parallel plates in oscillatory motion involves an ordinary differential equation while that for cone-and-plate testing requires the solution of a partial differential equation. In the solution for the equation of motion for the upper platen, fluid inertia, machine inertia, and machine viscous dampening were accounted for in a manner analogous to that of Walters [15] which accounted for only machine and fluid inertia. Using platen phase shifts and oscillation amplitude ratios, the complex viscosity can be calculated using the method of successive approximations. A computer program for this purpose was developed and is reported elsewhere [13]. Convergence was normally attained after 2 or 3 iterations.

RESULTS

Viscosity testing of solids-free coal-derived liquids

Viscosity testing showed solids-free coal-derived liquids from both H-Coal and SRC products to behave either as Newtonian fluids or to have a small amount of shear thinning occurring at higher shear rates. Figures 2 and 3

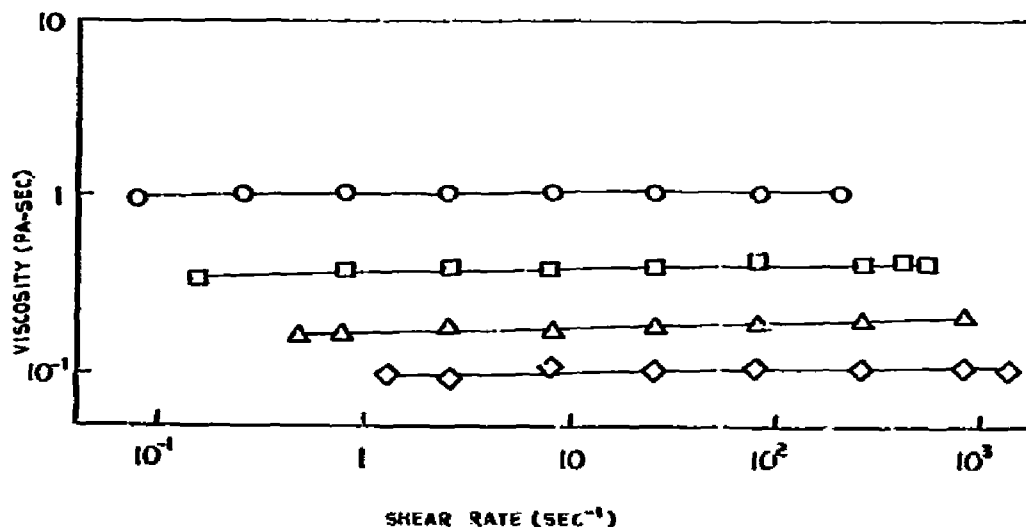


Fig.2. Apparent viscosity vs. shear rate for oils extracted from H-Coal vacuum-still bottoms residue. Testing temperatures: \circ , 22.2°C; \square , 32.4°C; \triangle , 40.8°C; \diamond , 49.0°C.

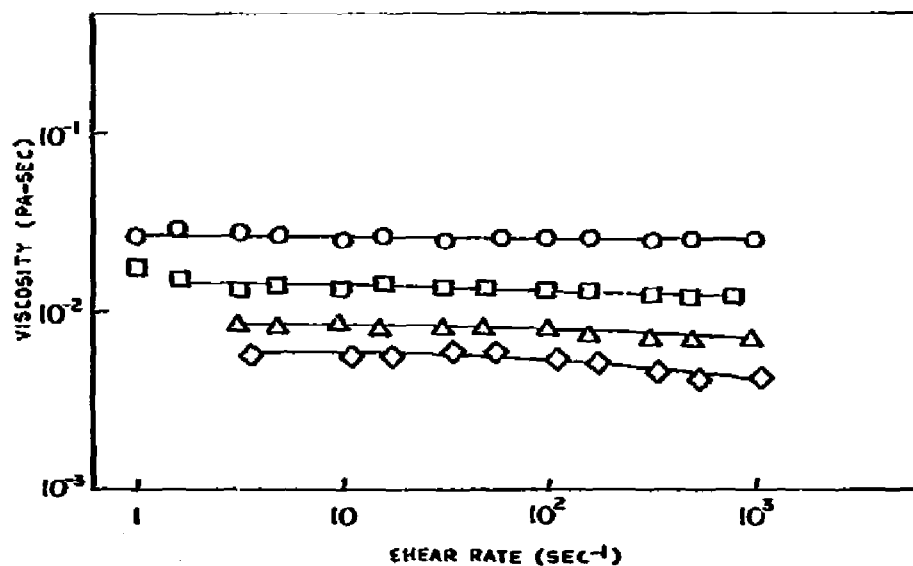


Fig.3. Apparent viscosity vs. shear rate for oils extracted from SRC whole product. Testing temperatures: \circ , 25.0°C; \square , 41.6°C; \triangle , 57.0°C; \diamond , 72.0°C.

show viscosity isotherms for H-Coal oils ranging over temperatures from 22 to 49°C and SRC oils over temperatures from 25 to 72°C, respectively, as functions of shear rate. A small amount of shear thinning is apparent for the SRC oils at higher shear rates and temperatures. Figure 4 shows the temperature effect on viscosity for these materials. This shows that plots of log vis-

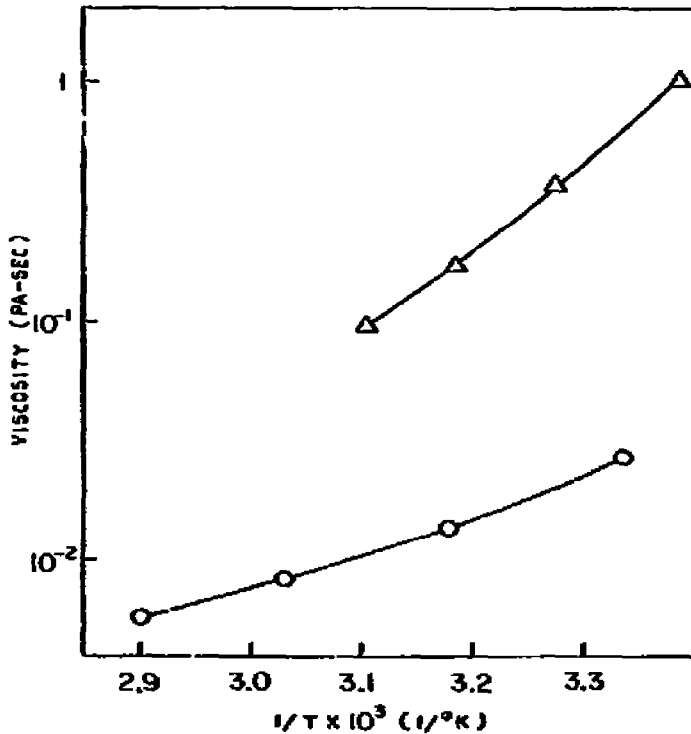


Fig.4. Apparent viscosity vs. the reciprocal of the absolute temperature. Δ , H-Coal oils at 10 (l/s) shear rate; \circ , SRC oils at 100 (l/s) shear rate.

cosity versus reciprocal temperature deviate from the traditional Arrhenius form given by:

$$\eta = A \exp(E/RT) \quad (2)$$

where η is the apparent viscosity, A is a constant, E is the flow activation energy, R is the real gas constant and T is the absolute temperature. The upward curvatures when going to lower temperatures are characteristic of associated fluids where intermolecular association becomes more prevalent [16, 17].

During testing of the less volatile fractions, such as asphaltenes or mixtures of oils, asphaltenes, and preasphaltenes, an experimental difficulty was encountered. It was found that at lower shear rates and higher temperatures, an "equilibrium" viscosity was established during a 15 to 45 min period. This "equilibrium" viscosity increased strongly with decreasing shear rate giving the appearance of pronounced shear thinning. This could either represent the true fluid behavior or be the result of some experimental artifact. The most likely experimental artifact would arise from a surface effect occurring at the fluid-air interface at the edge of the platens. Tests were done to evaluate the effect of this fluid-air interface. First, the fluid reser-

voir attachment (normally used for fluids of low viscosity) was utilized, which shifted the fluid-air interface from a vertical to horizontal attitude. Subsequent viscosity testing showed essentially Newtonian behavior at low shear rates. Next, the fluid was again tested without the reservoir attachment. After the usual "equilibrium" viscosity was attained, the outer portion of fluid to a depth of 2 mm was removed using a small probe. The viscosity was observed to fall to a value in accord with Newtonian behavior.

These tests indicated that a surface phenomenon was occurring. Tests were done to check the volatility of these coal-derived liquids. It was found that these samples can lose volatiles amounting to 1 to 4 weight percent in less than an hour at the temperatures used during viscosity testing. In addition to this surface devolatilization, it is possible that oxidation may be occurring, causing a chemical change in the surface material. However, the surface phenomenon was reversible to shearing. After attaining equilibrium at a low shear rate, if the sample were sheared at a high shear rate (greater than 100 s^{-1}) and then again at the low shear rate, the same time was required for equilibration.

It was therefore concluded that at higher temperatures, surface devolatiliza-

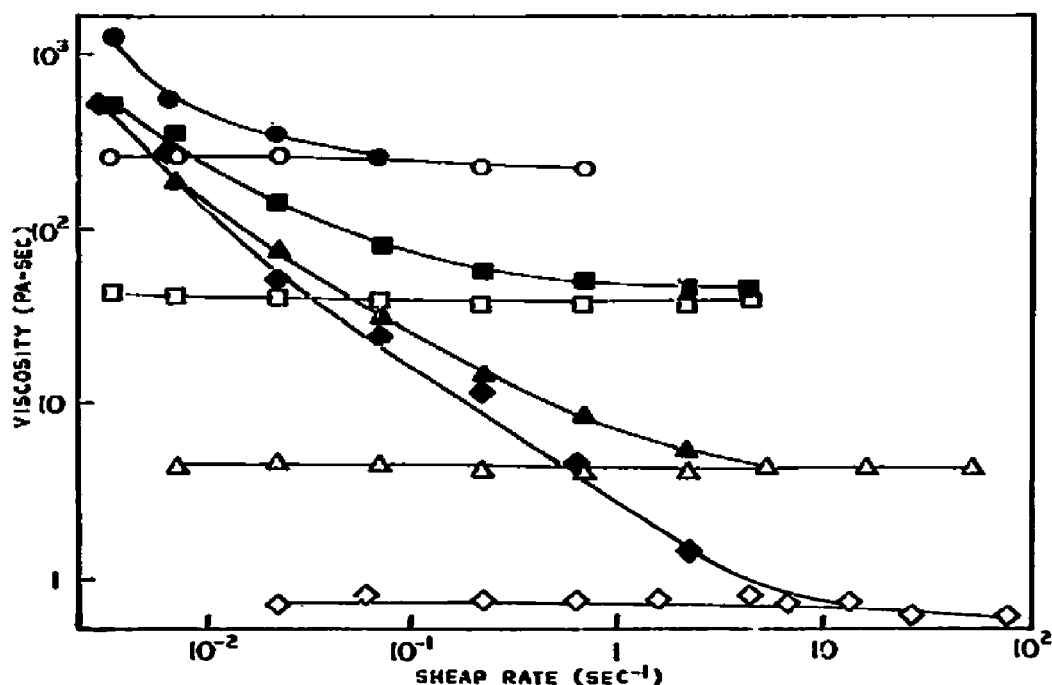


Fig. 5. Apparent viscosity vs. shear rate for asphaltenes extracted from H-Coal vacuum-still bottoms residue. The shaded symbols are the viscosities observed with the surface effect present. The unshaded symbols are the true apparent viscosities in the absence of surface effects. Testing temperatures: \circ and \bullet , 113.0°C ; \square and \blacksquare , 126.5°C ; \triangle and \blacktriangle , 145.5°C ; \diamond and \blacklozenge , 165.0°C .

tion and perhaps oxidation were producing a pseudoplastic surface film of greater viscosity than the bulk fluid. Altering the fluid surface to a horizontal attitude using the reservoir attachment reduced this surface phenomenon by exposing the fluid surface to radiation from the cooler Teflon top of the oven, as opposed to that from the much hotter band walls when in the vertical position. Removing the outer 2 mm of fluid after "equilibrium" effectively removed this surface film. Also, increasing shear rate eventually breaks down this surface film allowing one to take a viscosity measurement representative of the true fluid viscosity.

Figure 5 shows the viscosity data for H-Coal asphaltenes at four temperature levels. The "equilibrium" viscosities, representative of the surface effect, are shown with the true apparent viscosities to illustrate the shear rates and temperatures at which the surface effect becomes important. The true apparent viscosities were taken by preceding viscosity measurements with one minute periods of high shear rate to break down any surface film. Asphalt-

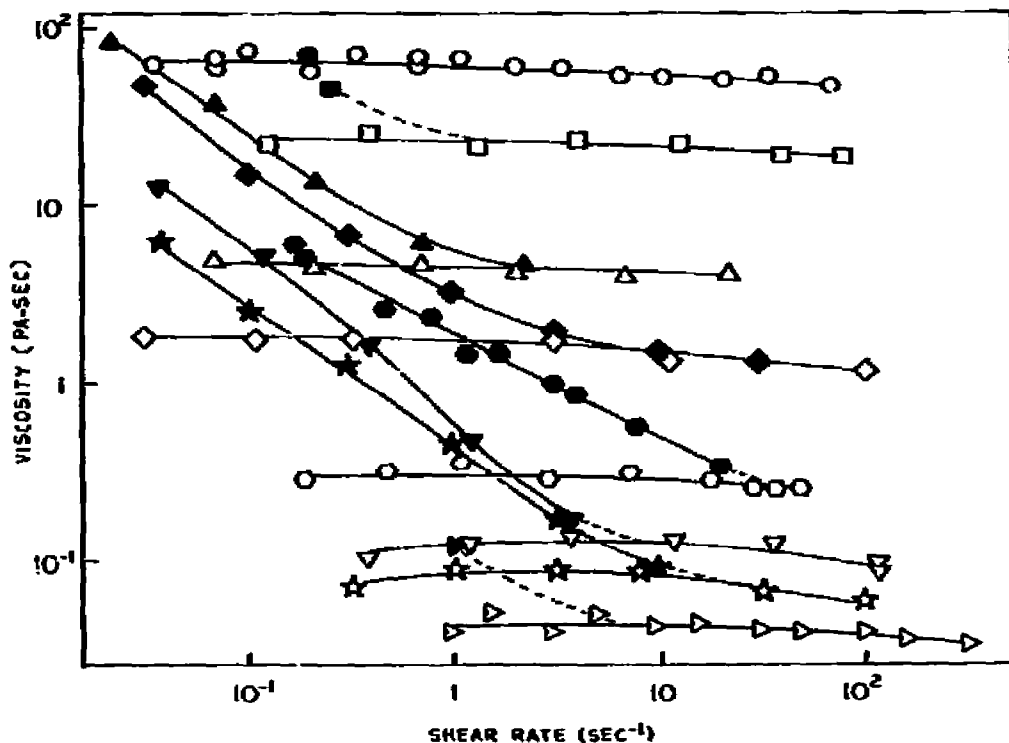


Fig.6. Apparent viscosity vs. shear rate at 165°C for solids-free mixtures of oils, asphaltenes, and preasphaltenes extracted from H-Coal vacuum-still bottoms residue. The weight ratio of asphaltenes to preasphaltenes was held constant at 2.59 while varying the oils content. The shaded symbols are the viscosities observed with the surface effect effects. The unshaded symbols are the true apparent viscosities in the absence of surface effects. Oils contents: ○ and ●, 0 wt.%; ◐ and ◑, 5 wt.%; △ and ▲, 10 wt.%; ◊ and ◆, 20 wt.%; ◌ and ◍, 35 wt.%; ▽ and ▾, 44 wt.%; ☆ and ★, 49.5 wt.%; ▷ and ◁, 54 wt.%.

tenes are seen to behave as Newtonian fluids except at higher shear rates and temperatures where slight shear thinning is evident. Figure 6 shows the viscosity data for mixtures of oils, asphaltenes, and preasphaltenes at 165°C. In these mixtures, the weight ratio of asphaltenes to preasphaltenes was held constant and the oils content was varied. The surface effect gives the appearance of shear thinning and is most pronounced at higher oils contents. The true apparent viscosities show relatively little shear thinning.

Viscosity testing of coal-derived liquids containing suspended solids

Viscosity testing of SRC whole product with a composition of 16.8 wt.% solids, 48.6 wt.% oils, 17.6 wt.% asphaltenes, and 17.0 wt.% preasphaltenes over a temperature range from 26.4 to 82.6°C showed little effect of solids on the fluid rheology. The viscosities were essentially Newtonian, showing a small amount of shear thinning at higher shear rates. No surface effects were evident at the low testing temperatures used. Figure 7 shows the effect of solids on viscosity-temperature behavior at a shear rate of 1.0 s⁻¹. Shown are the SRC whole product and the tetrahydrofuran soluble portion (the

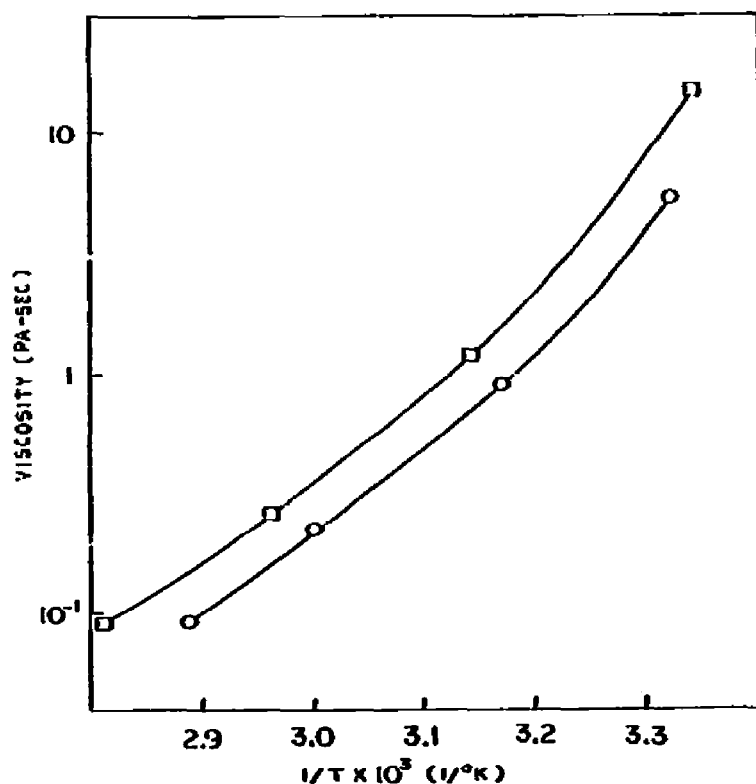


Fig. 7. Apparent viscosity vs. the reciprocal of the absolute temperature. □, SRC whole product at 1.0 (1/s) shear rate; ○, SRC THF solubles at 1.0 (1/s) shear rate.

SRC whole product minus the solids). The effect of the solids is to increase the viscosity by about a factor of 2. The volume fraction corresponding to 16.8 wt.% solids is about 0.11. Hydrodynamic considerations alone would predict viscosity to increase by a factor of ca. 1.34 [18]. This would imply that other viscosity-increasing phenomena such as electroviscous effects or solids flocculation could be acting to a small extent.

The rheological effect of solids when in H-Coal liquids was much more dramatic than when in SRC liquids. Figure 8 shows the viscosity isotherms for the unextracted H-Coal vacuum-still bottoms material. The composition of this material is 31.2 wt.% solids, 34.0 wt.% oils, 25.1 wt.% asphaltenes, and 9.7 wt.% preasphaltenes. Particle size distributions of these residual solids using the scanning electron microscope showed that about 95% of the solid particles had diameters less than $0.5 \mu\text{m}$. This suspension showed pronounced shear thinning and at the higher temperature levels, showed both low and high-shear viscosity plateaus. Tests showed that the viscosity of this material was not sensitive to surface effects over the range of temperatures and shear rates studied [13]. Therefore, this shear thinning is characteristic of the true fluid rheology rather than some surface phenomenon.

The effect of solids is more clearly seen by looking at Fig.9 which shows viscosity as a function of shear rate at 105°C . The weight ratio of liquids was held constant at 49.4 wt.% oils, 36.5 wt.% asphaltenes, and 14.1 wt.% pre-

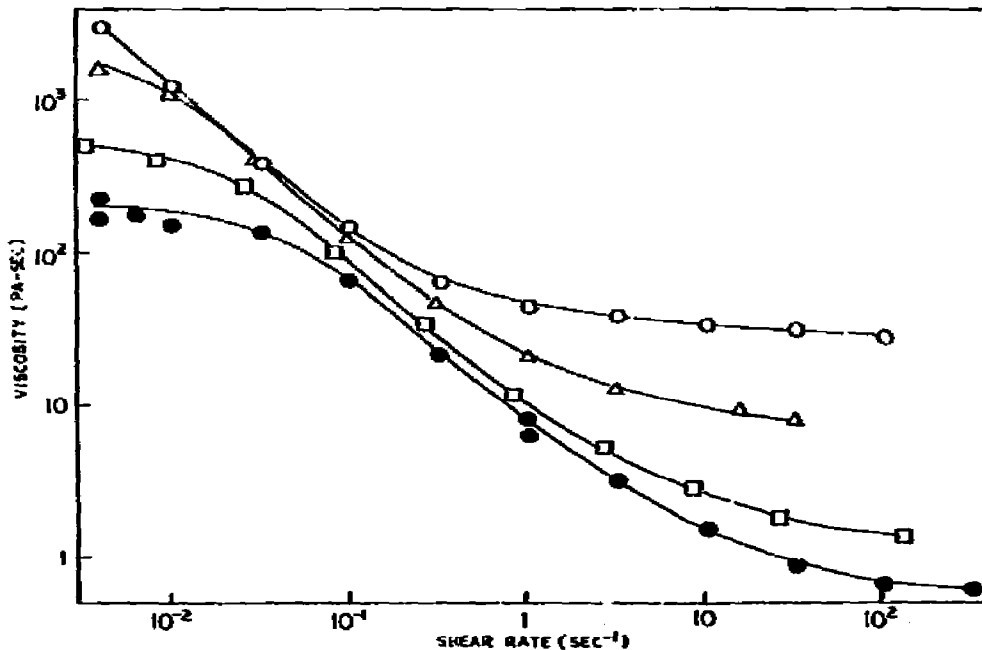


Fig.8. Apparent viscosity vs. shear rate for H-Coal vacuum-still bottoms residue (31.2 wt. % solids, 34 wt.% oils, 25.1 wt.% asphaltenes, and 9.7 wt.% preasphaltenes). Testing temperatures: \circ , 90°C ; Δ , 105°C ; \square , 124°C ; \bullet , 146°C .

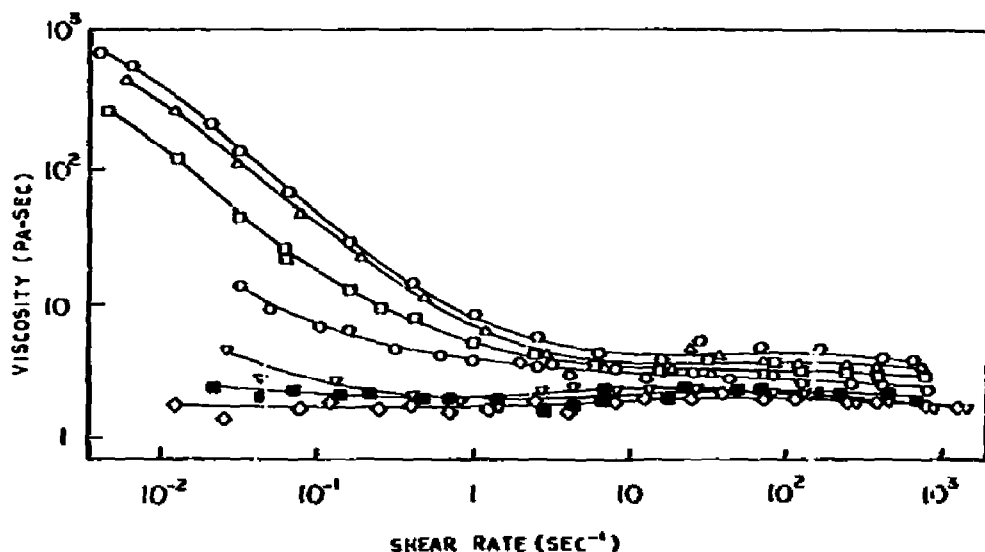


Fig.9. Apparent viscosity vs. shear rate for an H-Coal mixture of varying solids content with a constant liquid composition of 49.4 wt.% oils; 36.5 wt.% asphaltenes, and 14.1 wt.% preasphaltenes at 105°C. Solids weight percents: \circ , 0 wt.%; \square , 3 wt.%; ∇ , 7 wt.%; \diamond , 15 wt.%; \triangle , 25 wt.%; \blacktriangle , 28.5 wt.%; \circ , 31.2 wt.%.

asphaltenes. This weight ratio was chosen because it was the same as that of the unextracted H-Coal vacuum-still bottoms material. The composition of solids was varied from 0 to 31.2 wt.%. Shear thinning became evident at a solids content of 7 wt.% and became pronounced at compositions greater than 15 wt.%. At the low temperature of 105°C, no surface effects on viscosity were observed even for the 0 wt.% solids mixture.

Using the data in Fig.9, it becomes apparent that high shearing may disperse the solids in the H-Coal fluids. At a shear rate of 60 s^{-1} and 105°C, the viscosity as a function of weight fraction is shown in Fig.10. In the absence of any particle-particle interaction except hydrodynamic interaction, the viscosity should be a function of volume fraction only. Figure 10 shows hydrodynamic models of suspension viscosity up to the third order in volume fraction [19-21]. The third order theory is more than adequate to explain the observed increase in viscosity due to the presence of solids in H-Coal liquids at high shear rates. At lower shear rates, it is apparent that hydrodynamic models are not sufficient to explain the large increases in viscosity due to the solids. Other types of particle-particle interactions must dominate at low shear rates.

The shapes of the viscosity isotherms in Fig.8 are similar to those observed for some polymer materials. This suggested using the method of time-temperature superposition to obtain a master curve at some reference temperature [22, 23]. Using this method, the viscosity isotherms were shifted vertically and horizontally until the best overlap was attained with the 90°C

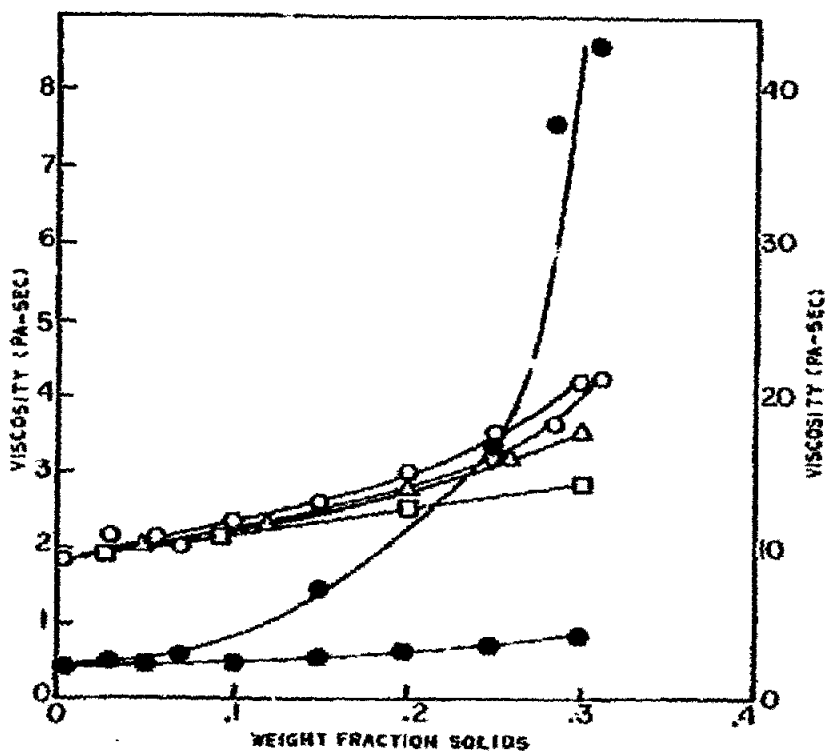
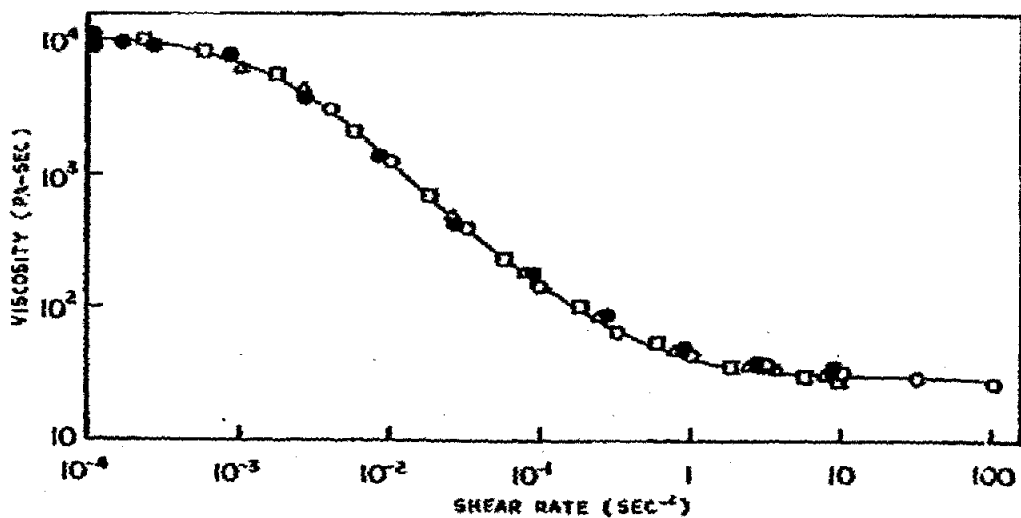


Fig.10. Viscosity vs. weight fraction solids in a mixture of H-Coal liquids having a constant composition of 49.4 wt.% oils, 36.5 wt.% asphaltenes, and 14.1 wt.% preasphaltenes and as predicted by various hydrodynamic models for suspension viscosity. Referred to the left ordinate scale: \circ experimental data at 105°C and 60 (l/s); \circ , Einstein's first-order hydrodynamic model, [19]; \triangle , Batchelor and Green's second-order hydrodynamic model, [20]; \circ , Lee's third-order hydrodynamic model, [21]. Referred to the right ordinate scale; \bullet , experimental data at 105°C and 0.1 (l/s); \bullet , Lee's third-order hydrodynamic model, [21].



isotherm which was chosen as the reference temperature. Figure 11 shows this superposition. Shape matching of curves was good. This gives a master curve at 90°C extending over six decades of shear rate with upper and lower shear-rate viscosity plateaus. Table 1 gives the shift factor a_T . If time-temperature superposition is valid, then it provides estimates for the zero-shear viscosities. These are also shown in Table 1.

TABLE 1

Time-temperature superposition of viscosity data to 90°C for H-Coal vacuum-still bottoms' material (31.2 wt.% solids)

Temperature shift (°C)	Shift factor a_T	Zero-shear viscosity (Pa·s)
90 → 90	1	9,031
105 → 90	0.254	2,279
124 → 90	0.066	461
146 → 90	0.070	190

A difficulty was encountered when measuring the viscosity of H-Coal suspensions at low shear rates and higher temperatures. If this measurement followed closely a period of high shear rate, an overshoot in torque or viscosity was observed. Figure 12 illustrates this with plots of torque versus time at different temperatures and at a shear rate of ca. 0.003 s^{-1} . At the lowest temperature, the torque developed to a steady value without any overshoot. At higher temperatures an overshoot was observed and the percent of overshoot increased with increasing temperature. These overshoots were not observed if viscosity data were taken by decreasing the shear rate in small steps. If shear rate were decreased in large steps (eg. a factor of 100) this overshoot could occur. A possible explanation for this phenomenon will be given in the discussion section.

Normal-force testing of H-Coal material

Representative samples of H-Coal material were tested for normal forces. In general, these fluids exhibited weak normal stresses. Because of this, testing was limited to higher shear rates, between 30 and 800 s^{-1} . In addition, experimentation was limited by a cyclical fluctuation in the total-normal-force reading (probably a surface tension effect) which became excessive at lower temperatures and small platen separations. When using parallel plates, platen separations were kept between 0.15 and 0.20 cm. Total

Fig. 11. Time-temperature superposition of apparent viscosity data from four temperature levels to 90°C for H-Coal vacuum-still bottoms residue (31.2 wt.% solids, 34 wt.% oils, 25.1 wt.% asphaltenes, and 9.7 wt.% preasphaltenes). Superposed isotherms: ○, 90°C; △, 105°C; □, 124°C; ●, 146°C.

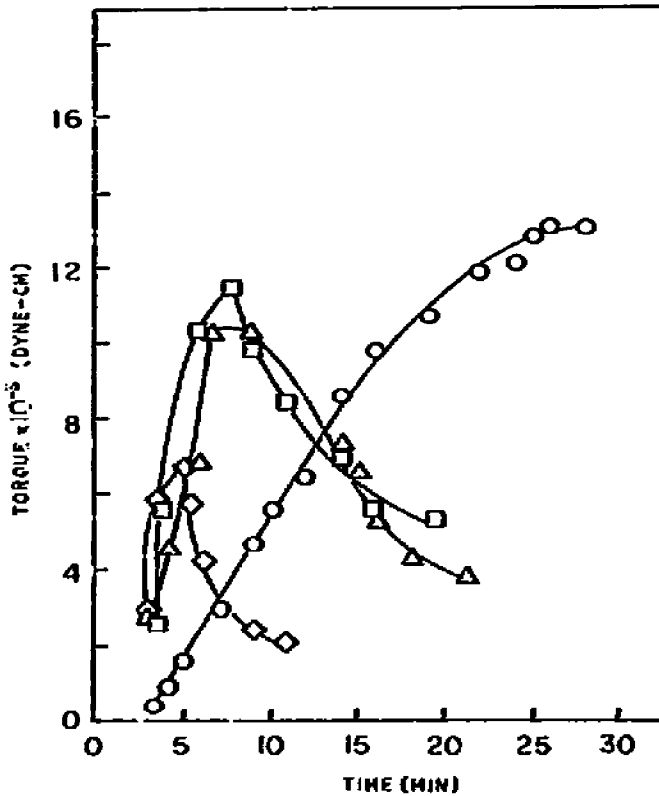


Fig.12. Development of torque during steady shearing at a shear rate of ca. 0.003 (1/s) following a period of high shear rate at ca. 100 (1/s) using H-Coal vacuum-still bottoms residue (31.2 wt.% solids, 34 wt.% oils, 25.1 wt.% asphaltenes, and 9.7 wt.% preasphaltenes). Testing temperatures: o, 90°C; □, 105°C; △, 124°C; ◇, 145°C.

normal forces decreased strongly with increasing temperature; however, the troublesome cyclical fluctuations became excessive at cooler temperatures which limited testing temperatures to a rather narrow range.

H-Coal oils showed no measureable normal forces between 23.4 and 40.0°C and up to shear rates of 800 s⁻¹. However, these oils are quite fluid at these temperatures and normal forces may become evident at cooler temperatures.

The less volatile H-Coal fluids showed distinct although weak normal forces. Figure 13 shows the first and second-normal-stress differences for the unextracted H-Coal vacuum-still bottoms material (31.2 wt.% solids) at three temperature levels. The first-normal-stress differences are positive and decrease with increasing temperature. The second-normal-stress differences are negative and are of magnitudes comparable to those of the first-normal-stress differences. The anomalous crossing over of the 101.5°C isotherm may reflect a viscous heating effect which was encountered when testing at low temperatures and at the highest shear rates.

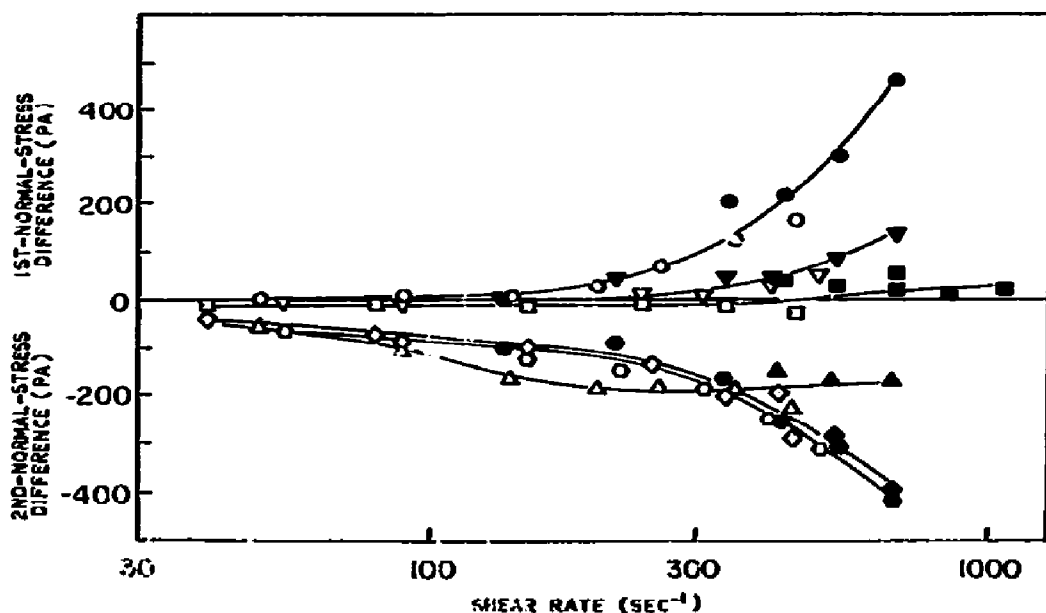


Fig.13. First and second-normal-stress differences vs. shear rate for H-Coal vacuum-still bottoms residue (31.2 wt.% solids, 34 wt.% oils, 25.1 wt.% asphaltenes, and 9.7 wt.% preasphaltenes). *First-normal-stress differences*: shaded symbols denote data taken using the cone-and-plate geometry, and unshaded symbols denote data taken using the extended cone-and-plate and parallel plate geometries. Testing temperatures: \circ and \bullet , 101.5°C ; ∇ and \blacktriangledown , 108.0°C ; \diamond and \blacklozenge , 114.0°C . *Second-normal-stress differences*: shaded symbols denote data taken using cone-and-plate and parallel plate geometries, and unshaded symbols denote data taken using extended cone-and-plate and parallel plate geometries. Testing temperatures: Δ and \blacktriangle , 101.5°C ; \circ and \bullet , 108.0°C ; \diamond and \blacklozenge , 114.0°C .

Figure 14 shows the normal stress differences for the solids-free H-Coal vacuum-still bottoms material (49.4 wt.% oils, 36.5 wt.% asphaltenes, and 14.1 wt.% preasphaltenes) at about 89°C . Looking at Figs.13 and 14, it can be inferred that the presence of solids acts to increase the magnitude of the normal stress differences. This was further substantiated by measurements of total normal force of these materials at comparable temperatures [13].

The first and second-normal-stress differences shown in Figs. 13 and 14 were calculated using total normal force measurements (F) corrected for the inertia forces (F_c). Table 2 shows values of $(F-F_c)$ taken using the various testing geometries as functions of shear rate for H-Coal material at 101.5°C and the solids-free H-Coal material at 89°C . Calculation of the normal stress differences from the cone-and-plate and parallel plate data is relatively straightforward [15]. When using the extended cone-and-plate geometry, however, it is necessary to test at several cone-and-plate separations (h) in order to determine the partial derivative of $(F-F_c)$ with respect to (h) . In this work, testing was done at three cone-and-plate separations and values of $(F-F_c)$ at a particular shear rate were plotted against (h) to determine this derivative. As can be seen from Table 2, this derivative had both positive and negative values.

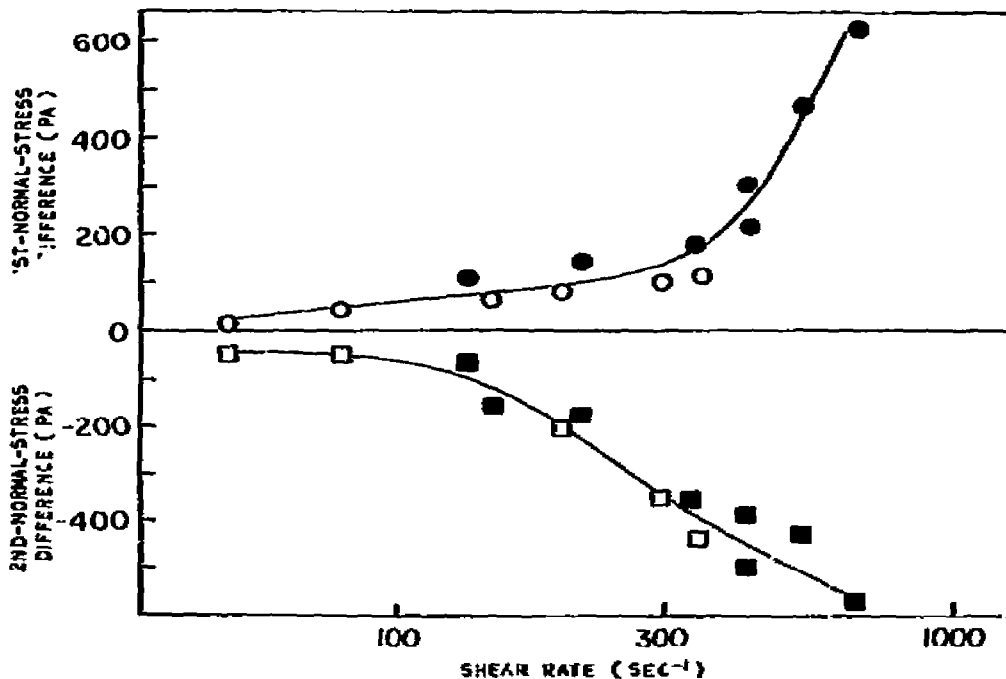


Fig. 11. First and second-normal-stress differences vs. shear rate for a solids-free mixture of H-Coal liquids with composition of 49.4 wt.% oils, 36.5 wt.% asphaltenes, and 14.1 wt.% preasphaltenes at 89°C. First-normal-stress differences were taken using the cone-and-plate geometry (shaded symbols) and using the extended cone-and-plate and parallel plate geometries (unshaded symbols). Second-normal-stress differences were taken using the cone-and-plate and parallel plate geometries (shaded symbols) and the extended cone-and-plate and parallel plate geometries (unshaded symbols).

TABLE 2

Total normal forces corrected for inertia ($F - F_c$) as a function of shear rate for various testing geometries

Cone-and-plate		Parallel plate		Extended cone-and-plate			
Shear rate (1/s)	($F - F_c$) (Pa)	Shear rate (1/s)	($F - F_c$) (Pa)	Shear rate (1/s)	($F - F_c$) (Pa)	$\left[\frac{5(F - F_c)}{5 - h} \right]_{h_1}$ (Pa/cm)	h_1 (cm)
(Material: H-Coal Vacuum-still bottoms at 101.5°C)							
215	3,509	41	513	50	1,050	-5,800	0.032
339	4,701	100	1,930	90	2,000	3,000	0.032
427	5,145	165	3,040	140	2,800	79,014	0.032
537	6,829	300	4,650	200	3,870	135,070	0.032
680	10,437	412	5,724	260	4,800	148,070	0.032
		522	7,224	350	5,980	138,000	0.032
				450	7,100	126,000	0.032
(Material: Solids-free vacuum-still bottoms at 89.0°C)							
136	2,567	70	600	50	500	-11,313	0.028
215	3,216	150	2,900	80	1,180	-18,460	0.028
215	4,202	300	6,300	150	2,560	-11,730	0.028
339	5,672	450	9,100	200	3,320	-13,811	0.028
428	6,934	650	15,000	300	4,960	-9,746	0.028
538	10,488			350	5,850	-3,372	0.028
681	13,920						

TABLE 3

Least squares slopes of log-log plots of the normal stress differences as functions of shear rate

Material	Temperature (°C)	Normal-stress differences	Least squares slope
Unextracted H-Coal	101.5	first	1.819
	108.0	first	2.150
	114.0	first	1.612
	101.5	second	0.614*
	108.0	second	0.708
	114.0	second	0.771
H-Coal asphaltenes	130.5	first	1.127
	130.5	second	1.226
H-Coal without solids	89.3	first	1.218
	89.3	second	1.136

*Only data from extended cone-and-plate and parallel plate geometries were used in the least squares fit

It is interesting to compare the slopes of log-log plots of the normal stress differences versus shear rate. Table 3 lists these slopes as determined by least squares fits for various materials. For the unextracted H-Coal suspension, the slope of the first-normal-stress difference was nearly 2, and that of the second-normal-stress difference was about 0.7. However, for the two solids-free liquids the slopes for both the first and second-normal-stress differences were about 1.2. Apparently, the presence of solids changes the qualitative behavior of the normal stress differences.

Oscillation testing of coal-derived liquids

Oscillation testing of H-Coal solids-free liquids showed these liquids to have little elasticity. Samples of oils, asphaltenes, and a mixture of 20 wt.% oils, 58 wt.% asphaltenes, and 22 wt.% preasphaltenes were tested at one temperature level over frequencies ranging from 0.03 to 60 Hertz. Dynamic viscosities (η') were frequency independent and were nearly equal to the steady-shear viscosities at the same temperatures. The dynamic rigidities (G') were essentially zero for frequencies less than about 3 Hertz. For higher frequencies there appeared to be an increase in G' but magnification of precision error made it difficult to interpret. It is possible that these fluids are weakly viscoelastic and show elastic character only at higher frequencies. Strains during oscillation testing were kept as low as possible, usually between 0.0146 and 0.076, in order to remain in the linear regime of viscoelastic testing.

Surface effects had to be circumvented when testing the asphaltenes (at

130°C) and the 20 wt.% oils mixture (at 165°C). A surface film formed at these temperatures over a period of 15–45 min, increasing η' and G' by over 2 orders of magnitude at the lowest frequencies. Successive testing at higher frequencies gave the appearance of a fall-off in η' and an increase in G' . Actually this was a manifestation of the viscoelasticity of the surface film. The true fluid dynamic behavior was found by interspersing frequency testing with one minute periods of steady shearing at ca. 100 s^{-1} . This acted to break up the surface film such that the true fluid complex moduli could be measured.

Oscillation testing of a representative coal-derived liquid with suspended solids was confined to testing H-Coal vacuum-still bottoms material (31.2 wt.% solids). Contrary to steady shear testing of this material, surface effects were evident in oscillation testing. The large deformations involved in steady shear testing together with the action of the solids must act to break down the surface film. Moreover, transient effects, as described for steady shearing, had to be accounted for in oscillation testing.

Testing was done at four temperatures ranging between 90 and 145°C. Testing was interspersed with one minute periods of steady shearing at about 100 s^{-1} to break down any surface film. At the highest temperature (145°C), oscillation testing was done 10 min. following this period of high

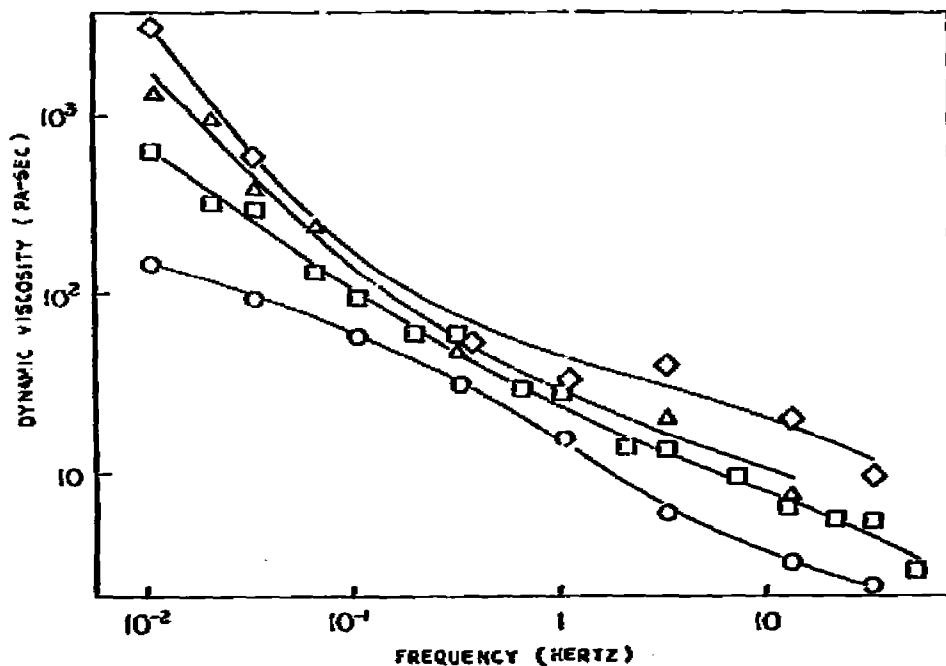


Fig. 15. Dynamic viscosity vs. frequency for H-Coal vacuum-still bottoms residue (31.2 wt.% solids, 34 wt.% oils, 25.1 wt.% asphaltenes, and 9.7 wt.% preasphaltenes). Testing temperatures: \diamond , 90°C; \triangle , 105°C; \square , 124°C; \circ , 145°C.

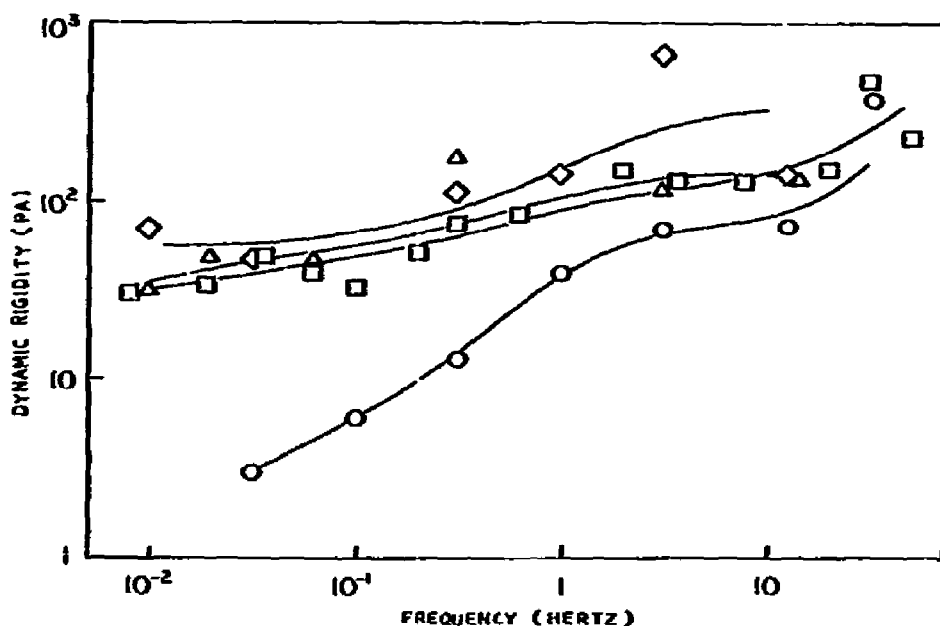


Fig.16. Dynamic rigidity vs. frequency for H-Coal vacuum-still bottoms residue (31.2 wt. % solids, 34 wt.% oils, 25.1 wt.% asphaltenes, and 9.7 wt.% preasphaltenes). Testing temperatures: \circ , 90°C; Δ , 105°C; \square , 124°C; \diamond , 145°C.

shear to allow the transient phenomenon shown in Fig. 12 to run its course (additional transient testing indicated that this transient phenomenon also occurred during rest periods following periods of high shear rate [13]). At lower temperatures, a longer period was necessary for this transient period to pass. At the lowest temperature, 90°C, a considerable time following high shear (on the order of an hour at the lowest frequencies) was necessary to establish representative values of η' and G' . The data acquired in this manner represent a compromise between testing times long enough to bridge the transient period and short enough to keep surface effects to a manageable level. These data are considered to be the "best estimates" given the circumstances.

Figs.15 and 16 show the "best estimates" of the dynamic moduli for H-Coal vacuum-still bottoms material at 90, 105, 124 and 145°C. The dynamic viscosities show a decrease with increasing frequency similar to the shear thinning behavior shown in Fig.8. The dynamic rigidities are significant down to frequencies of 0.01 Hertz. For all but the highest temperatures, the dynamic rigidities show a rather weak increase with increasing frequency.

Testing at various strain levels at 105°C showed the H-Coal vacuum-still bottoms material to behave in a nonlinear viscoelastic manner for strains greater than 0.1. The "best estimate" data were taken at strains less than 0.03.

DISCUSSION

In this study, coal-derived liquids without suspended solids behaved nearly as Newtonian fluids, with a small amount of shear thinning occurring at higher shear rates. The slight upward curvatures of plots of log viscosity versus reciprocal temperature indicate that coal-derived liquids may possess molecular structuring due to long-range association analogous to that found in highly polar liquids such as water. Also, judging from the varying chemical functionalities in different fractions of coal-derived liquids, it is likely that a certain amount of micellization may occur. The more aromatic and polar portions of these liquids may congregate to form a dispersed phase which would most likely be stabilized by a layer of lyophilic species. The small degree of shear thinning exhibited by these liquids supports the concept of a stabilized system rather than an unstable or flocculated system which would be more sensitive to shear.

Normal stresses are most commonly observed in polymeric systems or suspensions. The observation of normal stresses in solids-free coal-derived liquids which have relatively low molecular weights [4-6] is somewhat unexpected. Perhaps intermolecular interactions between polar groups or between aromatic groups play a role in the generation of these normal stresses.

The addition of solids (tetrahydrofuran insolubles) to H-Coal liquids resulted in elevated low-shear viscosities and pronounced shear thinning. Shear thinning in colloidal suspensions can arise from several causes. If the system is a stable dispersion, shear thinning can result from Brownian and/or electroviscous forces. Brownian motion can cause shear thinning in suspensions of nonspherical particles [24, 25] or in more concentrated systems by a mechanism involving doublet formation [26, 27]. Attempts to duplicate the viscosity shown in Fig. 8 using theories of Brownian motion proved inadequate [13]. Secondary electroviscous effects can also produce shear thinning in electrostatically stabilized suspensions [28, 29, 30]. Russel [31] developed a rigorous theory for finitely-dilute suspensions of charged spheres in homogeneous shear flow without inertia. Included in this theory are considerations of hydrodynamic, electrostatic, van der Waals and Brownian forces which provide the suspension with a microstructure. Qualitative trends from this theory such as normal stress differences which decrease to zero with increasing shear rate were not observed for H-Coal suspensions. Moreover, it is not clear how electroviscous or Brownian forces could cause the transient effects observed after a period of high shear rate (Fig. 12).

The most intuitive explanation for shear thinning of the H-Coal suspensions would be to assume the suspension to be unstable and to form loose flocs. During shearing, a dynamic equilibrium between flocculation and shear-induced deflocculation would develop. At low shear rates flocculation would dominate, producing large flocs and immobilizing relatively large amounts of solvent. As shear rate increases, the flocs would be progressively broken

down, liberating solvent, and thus decreasing the apparent viscosity. At high shear rates, the suspended solids would be well dispersed and the viscosity would be that as predicted from particle-volume-fraction considerations alone. This was observed and is implied in Figs.9 and 10.

An estimate of the floc volume fraction at very low shear rates for the H-Coal vacuum-still bottoms material was made. Using the solvent viscosity at 146°C (0.146 Pa-s) and the zero-shear viscosity at the same temperature (190 Pa-s as shown in Fig. 8) the relative viscosity is 1301. The empirical correlation for relative viscosity as a function of dispersed phase volume fraction developed by Thomas [32] was used to calculate an effective floc volume fraction of 0.79. Assuming an actual particle volume fraction of 0.224, this implies that 71.6% of the floc volume is trapped solvent.

The existence of a finite zero-shear viscosity would imply that this suspension when at rest is a sol rather than a gel. At the lowest temperatures, the viscosity was not observed to level off at low shear rates but, if time-temperature superposition is a valid indicator, one would expect finite zero-shear viscosities at lower shear rates. Most likely, thermal convection currents are sufficient to keep the flocs from forming a continuously-linked network.

If the H-Coal suspensions were flocculated, an explanation for the torque overshoot following periods of high shear could be made. Following a period of high shear, the solids were well dispersed. Initial flocculation may proceed to form rather long strands or chains of particles [33, 34] which may form initially very loose-knit flocs. If shearing were conducted at low enough shear rates and high enough temperatures (giving a lower solvent viscosity), the hydrodynamic force would not be enough to disrupt this floc and a high value of viscosity would be observed. However, random thermal motion (Brownian motion) may eventually reorganize these flocs to form more consolidated flocs with less trapped solvent, and thus, less viscosity. This process would occur at very low shear rates or at rest, as was experimentally observed.

The above argument can be used to explain the time-temperature superposition of viscosity in Fig.11. At higher temperatures, the flocs are more resistant to shear-induced break-up since the solvent viscosity is less and the flocculation rate is greater. Therefore, the high shear-rate viscosity plateau would be observed at higher shear rates for higher temperatures.

The experimental observation of the weak frequency dependence of dynamic rigidity is also in keeping with the notion of a flocculated H-Coal suspension. Theories for viscoelastic behavior of suspensions have been developed and tested [35, 36] which have indicated a constant G' with varying frequency.

CONCLUSIONS

Rheological testing of coal-derived liquids using rheometers which expose the test fluid to the atmosphere can be significantly affected by a surface "film" which develops on the fluid-air interface. This is in part due to sur-

face devolatilization and perhaps oxidation and is more pronounced at higher temperatures. Shearing the material at high shear rates temporarily breaks down this surface film allowing rheological measurements to be made. This surface film was a problem during steady shear and oscillation testing of solids-free coal-derived liquids but it was only a problem during oscillation testing for coal-derived liquids with suspended solids. Apparently, the solids disrupt this surface film during steady shearing. The surface film was no problem during normal force testing because testing was confined to high shear rates.

Solids-free coal-derived liquids obtained from SRC and H-Coal liquefaction processes showed either Newtonian viscosities or slight shear thinning occurring at higher shear rates. The variation of viscosity with temperature in coal-derived liquids indicates that these liquids behave as associated liquids. Oscillation testing indicates that these liquids are, at most, weakly viscoelastic. Normal-force testing showed the less volatile solids-free coal-derived liquids to have measureable normal stress differences.

The presence of suspended residual solids in coal-derived liquids can significantly alter the rheology of these fluids. In the case of H-Coal suspensions, the viscosity increased dramatically at low shear rates and pronounced shear-thinning resulted. The presence of suspended solids also increased normal stresses and imparted a definite viscoelastic quality to the fluid. From these results and from the transient behavior following periods of high shear rate, it is concluded that residual solids in these H-Coal fluids form an unstable colloidal suspension with the degree of flocculation largely dependent on flow conditions. At very low shear rates, the residual solids form loosely-knit flocs which are readily disrupted by shear rate giving the shear-thinning effect. However, this is not meant to imply that solids have this effect in general for coal-derived liquids. The presence of solids in SRC liquids did little to change the fluid rheology, i.e., it behaved as a stable suspension. The stability of suspensions of residual solids in coal-derived liquids is dependent on many factors. Rheological testing is one way to detect this stability.

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