The Expanding Dimensions of High Shear Rate Viscometry

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ABSTRACT

Viscometry has been closely associated with the lubricating properties of engine oils since the development of the reciprocating engine. With the advent of non-Newtonian multi-grade engine oils, a new dimension of viscometry was introduced – viscometry at high shear rates and high temperatures.

In view of the importance of the critical hydrodynamic lubrication that engine oils provide – and the toll on engine efficiency that these oils extract – it was thought timely and practical to review the initiation and application of high shear rate engine oil viscometry and to discuss subsequent development.

INTRODUCTION

Fundamentally, viscosity is resistance to flow – as a form of friction generated by the physics and chemistry of the molecules of a liquid moving past one another as the fluid is forced to flow.

Since the development of the reciprocating engine, viscosity of the engine oil has always been recognized as its most important property in avoiding catastrophic failure. At operating temperatures – depending on the design and power of the engine – sufficient resistance to flow (viscosity) is necessary to obtain the desired hydrodynamic thickness of the oil film formed between loaded surfaces in relative motion such as occurs between journals and their bearings.

BACKGROUND

NEWTONIAN VISCOMETRY - So-called 'straight grade' engine oils (for example, an SAE 30 with the '30' being a simple number signifying a relatively moderate level of operating viscosity) were established early in the development of the J300 Viscosity Classification System of the Society of Engineers [Ref 1,2]. These oils were Newtonian in character (that is – at a given temperature – viscosity is constant at any shear rate). Thus, for such oils, low shear rate viscometry gave adequate information regarding the hydrodynamic properties needed and such information could be obtained by simple capillary viscometry.

TEMPERATURE DEPENDENCE OF VISCOSITY - One of the more difficult properties of engine oils to surmount is the natural exponential increase in viscosity with decreasing temperature. The level of viscosity needed for effective hydrodynamic lubrication at higher engine operating temperatures makes it comparatively difficult to start the engine at lower temperatures where viscous friction impedes the motion of engine components.

MULTIGRADE OILS

In the 1940s, a major development in engine oil formulation reduced change of viscosity with temperature and improved low-temperature engine starting – an effect accomplished by the addition of relatively small amounts of oil-soluble, higher molecular weight, polymers in engine oil formulations using somewhat lower viscosity base oils. This development led to a class of oils defined by the term 'multi-grade' which today constitute the majority of marketed engine oils in developed countries. The term 'multi-grade' was meant to suggest that such oils as SAE 10W-30 would ease lower temperature startability (the '10W' grade designation) while still providing acceptable levels of viscosity for hydrodynamic lubrication (the '30' portion of the grade designation).

MULTI-GRADE ENGINE OILS AND THEIR HIGH SHEAR RATE RHEOLOGY – Interestingly, introduction of multi-grade engine oils directly led, in time, to the need to develop understanding of their high shear rate and high shear stress viscosities which, of course, play a critical role in their ability to provide hydrodynamic lubrication. The dissolved polymer in these oils made them non-Newtonian in behavior. That is, they possessed viscosities that varied not only with temperature but with shear rate and shear stress. This interrelationship between multi-grade engine oils and high shear rate/stress viscometry is at the heart of this paper.

Measurement of the flow phenomena of such systems is essentially the only experimental information available to interpret the rheological behavior of these multi-grade engine oils. Theoretical efforts to form equations agreeing with the physical data of polymer solutions have had some degree of success.

HIGH SHEAR RATE VISCOMETRY OF MULTIGRADE ENGINE OILS

INTEREST IN HIGHER SHEAR RATE VISCOMETRY – The benefits of multi-grade engine oils in starting the engine at lower temperatures was apparent to many automobile owners and the popularity of such engine oils grew rapidly.
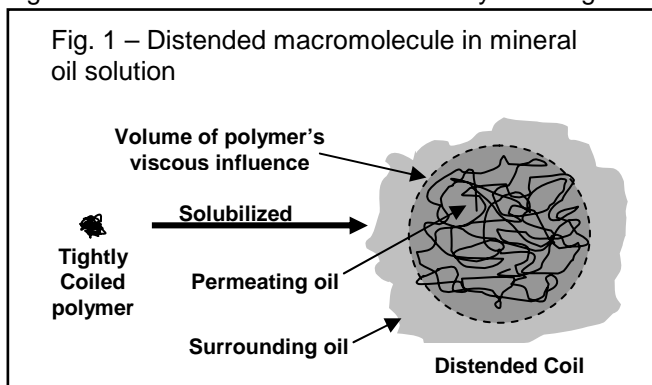
There were other considerations, as well. For example, on a more technical level, there was uncertainty about the effective viscosity of these multigrade lubricants at engine operating temperatures [1]. This uncertainty arose when studies of polymer-oil solutions [3,4] showed that their viscosities decreased recoverably with increasing shear rates and also decreased unrecoverably with time in engine service [5,6]). Thus, in regard to multi-grade engine oils, simple low shear viscometry was no longer considered sufficient to define the engine oil viscosity and its associated level of hydrodynamic lubrication and engine protection.

PHYSICS OF POLYMER-CONTAINING OILS

Shear-sensitive viscometric behavior is an interesting physical response of oil-soluble macromolecules to flow at high shear rates and stresses and/or before and after cavitation conditions. Such non-Newtonian response is believed related to the physical configuration of the solvated polymeric macromolecules. The rheological response of these fluids makes the following hypotheses helpful in conceptualizing the high shear rate viscosity loss for the linear and nearly linear macromolecules used in VI Improvers (i.e., those having a very large molecular length to width ratio when uncoiled) as well as other forms of polymers that are distended in solution.

VISCOSITY CHANGE WITH POLYMER SOLUTION – Small quantities of dissolved polymer have a strong effect on the oil's resultant rheological response under shear. Each macromolecular coil is believed to be greatly distended when solubilized by the oil as shown in Figure 1, depending on the temperature, molecular weight, distended size of the macromolecule, and degree of polymer solvency of the particular base oil [7].

Considering the nature of polymer solution and the restrictions imposed by its intermolecular bonds, the degree of coil distention is increased by the degree of

Fig. 1 – Distended macromolecule in mineral oil solution

Volume of polymer's viscous influence

Tightly Coiled polymer

Solubilized

Permeating oil

Surrounding oil

Distended Coil

similarity of the macromolecular composition to that of the oil molecules. With this understanding, some VI Improvers are designed to contract progressively in response to lower oil temperatures and *vice versa*. This reduces oil viscosity at low starting temperatures. In comparison, other VI Improvers retain a high level of solubility over a considerably wider temperature range. Both forms of solubility have advantages as will be seen.

QUIESCENT AND FLOWING POLYMER SOLUTIONS – The flexible solubilized polymer molecule takes different configurations depending on whether the oil containing the dissolved polymer is quiescent or flowing.

Quiescent Polymer Configuration – As shown in Figure 2, when the polymer-containing fluid is quiescent in a relatively energy-relaxed state, theory indicates that the distended coil assumes a spheroidal shape having Gaussian chain-link distribution across the particle [7] and is surrounded and permeated by the oil molecules.

Flowing Polymer Configuration – However, since viscosity is fluid friction at the molecular level, any motion of the fluid mass imposes inter-molecular frictional forces on, and by, all fluid molecules and dissolved macromolecules. That is, the macromolecular coil both influences the flow of the surrounding and permeating small molecules of the fluid and is also caught in their collective and interactive viscous 'grip'.

Flow at Very Low Shear Stresses – At a given temperature and at relatively low shear stresses, the integrity of the polymer sphere is maintained by its intra-molecular bond constraints. Under these conditions the fluid mass demonstrates Newtonian behavior (viscosity is constant at different low stress levels). This has been called the 'First Newtonian Region' of flow.

Flow at Higher Shear Stresses – The distended polymer molecules create additional flow resistance and, thus, a significant increase in viscosity above that of the base oil. However, the macromolecule occupies many contiguous flow planes of the smoothly moving, solvating oil. If the shearing force (shear stress) is increased, at some level that stress will exceed the strength of macromolecular bonds to resist deformation and the macromolecule will begin to lose the spherical symmetry it has when quiescent or moving slowly with the fluid.

Under higher stresses the various local and overall stresses applied to the macromolecule by the viscous 'grip' of the surrounding and permeating fluid molecules, will then extend and orient the macromolecule along the flow path of the fluid mass, transforming the spherical macromolecular form into the prolate form shown in Figure 2. In such form, as the macromolecule is distended more and more by the applied stress, the polymer coil is less and less effective in retarding mass flow and the total fluid mass consequently becomes less viscous. Rotation of the coil shown in Figure 2 has been postulated in theoretical studies and calculations [8].

Fig. 2 – Distortion of macromolecule in the shear gradient of a laminarly flowing polymer-in-oil solution

Solid surface

Rotating

Shear

Quiescent

Coil in flow
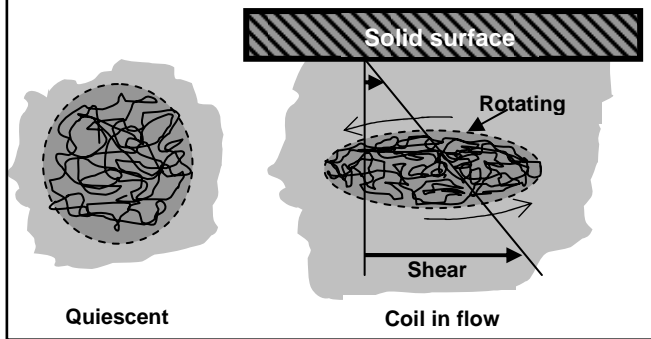
However, at sufficiently high shear stress, further compression of the now prolate polymer coil is resisted by the bonds and steric hindrances of the now very distorted and folded macromolecule. Consequently, a level of shear stress is reached at which no further distortion and elongation can be applied by the viscous 'grip' of the solvating oil and the viscosity is once again unaffected by increase in shear stress. This region of flow of the solubilized polymer in oil has been called the 'second Newtonian Region'.

Figure 3 shows the entire flow curve for a low-concentration of solubilized polymer in oil. This response has been well confirmed by several viscometric studies [9,10,11].
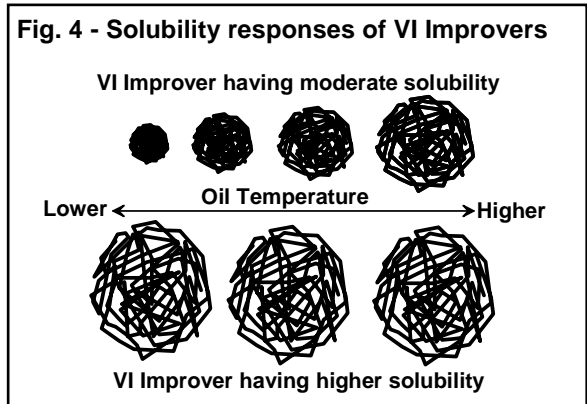
It should be noted that the level of force applied to create such macromolecular orientation is usually far less than the force necessary to break its molecular bonds. Thus, the polymer coil recovers its shape when the shearing force is relieved and the earlier viscosity level is recovered. This response of a polymer-containing oil is termed 'temporary viscosity loss' (TVL) and, for comparison of TVL values, is often presented as %TVL.

POLYMER SOLVENCY – The degree to which the macromolecule can be distorted is also influenced by the degree of solvency it has in the base stock (i.e., the degree of distention the macromolecule assumes).

As previously noted, all polymers used as VI Improvers do not have the same degree of solubility in a given base
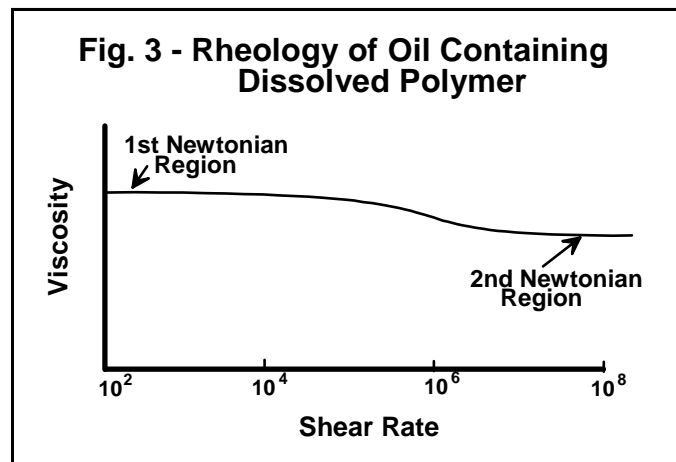
oil. Oil solubility of some polymers decrease with decreasing temperature as indicated in Figure 4.

Fig. 4 - Solubility responses of VI Improvers

VI Improver having moderate solubility

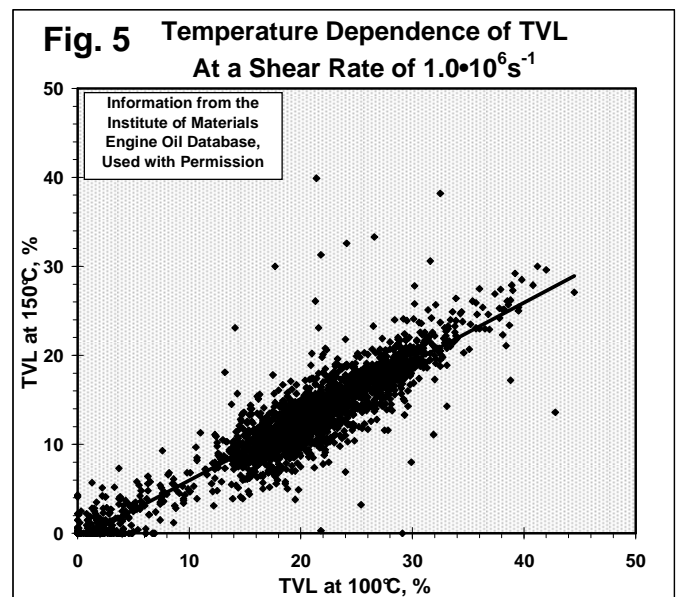Lower ← Oil Temperature → Higher

VI Improver having higher solubility

Thus, as previously noted, the polymer becomes much less extended and consequently the polymer's viscosity-contribution is less at lower temperatures [12]. This is can be advantageous in startability.

Other VI Improvers are more soluble and tend to retain this solubility at lower temperatures. Depending on molecular weight and polymer concentration, the more oil-soluble the polymer, the more efficient it is in increasing both the oil viscosity and its Viscosity Index.

Flow Orientation, Solubility, and Temperature – As shown in Figure 4, highly soluble polymers tend to retain their degree of solubility with temperature change. This affects the %TVL observed at different temperatures. When temperature of the oil is lowered, its viscosity as well as its viscous 'grip' on the macromolecules naturally increases. Consequently, greater shear orientation of the macromolecule will result at lower temperatures. This response is shown in Figure 5 obtained from data published in the Institute of Materials Engine Oil Databases [13], in this case, for North America.

The %TVL data in Figure 5 are obtained at both 150°

Fig. 3 - Rheology of Oil Containing Dissolved Polymer

1st Newtonian Region

2nd Newtonian Region

Viscosity

10^2 10^4 10^6 10^8

Shear Rate

Fig. 5   Temperature Dependence of TVL At a Shear Rate of $1.0 \cdot 10^6 s^{-1}$

Information from the Institute of Materials Engine Oil Database, Used with Permission

TVL at 150°C, %

TVL at 100°C, %

and 100℃ and it is interesting to note that

1. the best line through the data shows that %TVL is increased by about 30% at 100℃, and
2. most of the 2000+ values shown are gathered in a relatively close-fitting band (R^2=0.82) about the best line through the data, particularly from 12% to 35%TVL.

This information indicates that most of the multi-grade engine oils in North America contain varying amounts of relatively soluble VI Improvers and that the molecular weight distributions of these macromolecules are high enough to produce a 30% gain in %TVL when the temperature of low and high shear rate viscosity measurements is decreased from 150° to 100℃.

PAST RANGES IN HIGH SHEAR RATE VISCOMETRY

GENERAL – With the advent of multi-grade engine oils, it became evident that high shear rate measurement of the viscosity of these polymer-containing oils was important to those concerned with automotive engine oil. In 1975, SAE accepted and defined the multi-grade category of 15W as a note in the SAE J300 Viscosity Classification System and in 1977, SAE requested ASTM International to develop a method of measuring the viscosity of multi-grade oils at high shear rates of $10^6 s^{-1}$ and a temperature of 150℃ [14].

CHOICE OF INSTRUMENTATION GEOMETRY – On the basis of rheological experience, only two instrumental geometries were considered practical and applicable for the purpose of measuring viscosity of oils at constant temperature and various but suitably high shear rates. These two geometries were the capillary viscometer and the rotational viscometer. Both geometries had been used experimentally at high shear rates and at various temperatures [15,16,17,18,19]. However, when applied to polymer-containing, non-Newtonian fluids, these two geometries produce considerably different non-Newtonian response as a consequence of very different shear rate profiles across the flowing fluid.

As shown in Figure 6, in capillary viscometry, at a given flow rate, shear rate is not constant but rather ranges from maximum value at the wall to zero at the peak of

Fig. 6 - Comparison of Geometries

Capillary tube   Stator   Rotor

Oil   Flow Profile   Oil

Change in shear rate:

dv/dr=high

dv/dr=zero

velocity of flow   v

Stationary   v   rate of rotation

r r   r

Capillary Geometry   Rotational Geometry

the presumed parabolic flow profile. Note that the flow profile of polymer-containing oils is not parabolic as a consequence of the effect of the varying shear rates across the tube on the polymer coil. This limits high shear rate studies of polymeric solutions in oil [20,21].

In comparison, concentric or near-concentric cylinder viscometry with matching rotor-stator geometry produces an essentially constant shear rate throughout the fluid being sheared in the rotor-stator gap. With this advantage of constant shear rate and greater control of temperature, as well as no pressure or end effect corrections of the capillary, rotational viscometry is the geometry of choice for investigating the shear dependence of polymer-containing oils as indicated by most of those choosing to do research in this area.

High Shear Viscometer Development – In response to the SAE's 1977 request to ASTM for viscometry to generate $1.0 \cdot 10^6 s^{-1}$ at 150℃, the Paramins division of Exxon commissioned the development of what became the rotational Tapered Bearing Simulator (TBS) Viscometer [22]. This instrument was developed to make a relatively simple high shear rate viscometer generally available for laboratory use. The instrument reflected some of the early work of Kingsbury [15] with a slightly tapered rotor and the more recent work by Pike [18] and his associates, also using a tapered rotor.

Later, another tapered rotor viscometer was introduced [23] that also used a tapered rotor. Still later, a high-pressure capillary viscometer was introduced [24].

A multi-instrument, ASTM round robin involving all three commercial instruments [25], showed that the two commercial tapered rotational viscometers agreed well but that the high-pressure capillary did not. Regarding the latter, Kroepelin's much earlier equation [26] correctly predicted the average shear rate would be about 2/3 that at the wall for a Newtonian fluid. The multi-instrument ASTM round robin indicated that a value of $1.4 \cdot 10^6 s^{-1}$ at the capillary wall gave multi-grade oil viscosity values equivalent to the viscosity values from the constant-shear-rate rotational viscometers. This one corrective value of $1.4 \cdot 10^6 s^{-1}$, however, assumed that all polymer-containing, multi-grade oils will have approximately the same flow profile which, as previously noted, is an approximation because the different response to the shear gradient across the capillary of various VI Improvers.

In 1992, based on an ASTM status report [27] and a following ASTM symposium [28], SAE modified the J300 Viscosity Classification System to specify viscosities of oils at $10^6 s^{-1}$ and a temperature of 150℃ [2].

Application of the TBS Viscometer – The rotational Tapered Bearing Simulator Viscometer is the only viscometer capable of producing the very high shear rate and wide temperature range information desired for the investigations reported in this paper.
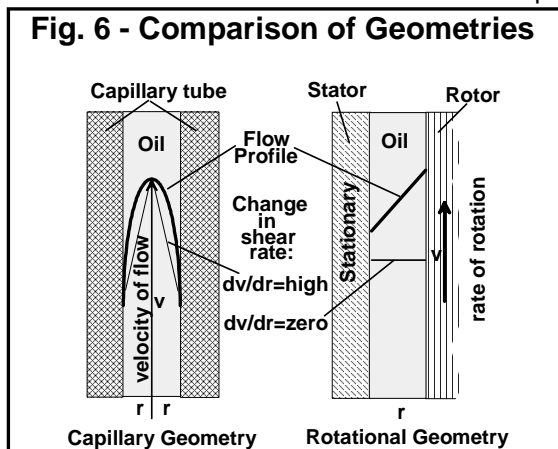
The essential components of the TBS Viscometer are shown in the sketch of Figure 7. One of the advantages of the instrument is in being able to precisely set rotor position (and, thus, shear rate) while the instrument is operating which allows operation at any temperature as an absolute viscometer as will be shown. Another is to set rotor speeds at 12 levels from 800 to 8000 RPM while operating. This has enabled reaching much higher shear rates than $10^6 s^{-1}$.

Fig. 7 -- Sketch of TBS Viscometer rotor-stator geometry
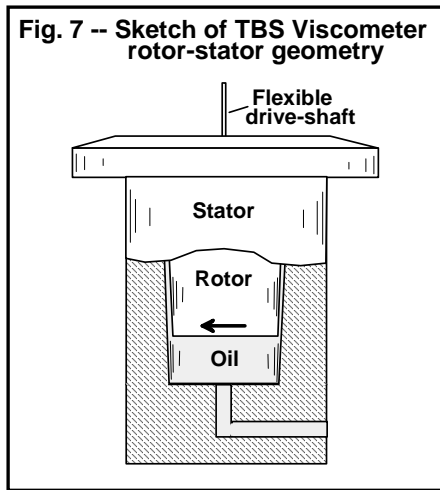
MODERN VERY HIGH SHEAR RATE AND VARIABLE TEMPERATURE ANALYSES

GENERAL – Viscometry at very high shear rates and lower temperatures and thus higher viscosities (higher viscous friction), requires greater control of the heat generated to obtain constant operating temperatures.

Temperature Control – Both viscosity and, particularly, the shear rate combine to frictionally heat the fluid being analyzed according to the equation

$$H = \eta \bullet \dot{G}^2 \qquad \text{(Eq. 1)}$$

in which **H** is frictional heat energy, η is viscosity, and $\dot{G}$ is the shear rate [20].

Very High Shear Rates – The original request made by the SAE of the ASTM for measurement of engine oil viscosity at $10^6 s^{-1}$ and 150℃ was all that was thought to be accomplishable at the time. However, since that time, further development of the TBS Viscometer to include a broad speed range has permitted evaluation of engine oils and other fluids at both lower and considerably higher shear rates by setting the rotor gap at a desired shear rate and multiplying or dividing this shear rate by changing rotor speed.

Other Temperatures – Similarly, recognizing that it is desirable to measure high shear rate viscosity at other temperatures, circulating coolant has been applied to the TBS Viscometer and this has allowed high shear rate viscosity measurement as low as 40℃ with viscosities as high as 30 mPa•s (cP).

VERY HIGH SHEAR RATES – It has been well known that actual operating shear rates in the engine were much higher than $10^6 s^{-1}$, but it was hoped, and later shown (28), that $10^6 s^{-1}$ shear rate would at least give clear and meaningful correlation with the operating engine.

Evidence of Correct High Shear Rate Viscometry – Meaningful high shear viscometry requires certainty that the instrument is capable of controlling temperature and shear rate. A viscometer claimed to have the ability to provide high shear rate performance can be made to show evidence that it can. This is done by providing correct and consistent information by analyzing a series of Newtonian oils of different viscosities at a given temperature. According to Newton's linear equation [29] for all simple (Newtonian) fluids:

$$\eta = \tau/\dot{G} \quad \text{or} \quad \eta = cT/\dot{G} \qquad \text{(Eq. 2)}$$

in which η is viscosity, τ is shear stress, $\dot{G}$ is shear rate. If **T** is rotor torque, **c** is the constant of proportionality when using **T**. Thus, a plot of rotor torque versus shear rate for a series of Newtonian oils should form a series of straight lines passing through the data sets all of which lines converge at a common origin (the origin value showing any non-viscous, mechanical friction of the instrument).

Figure 8 presents such data from a multi-speed improvement [30] of previous multi-gap studies [31] on five Newtonian reference oils at 150℃ by using a series of 12 rotor speeds from 800 to 8000 RPM.
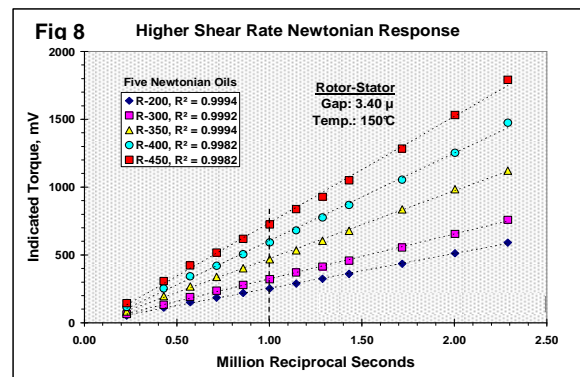
It is evident that the viscometer gives the precise Newtonian response expected from Equation 2 with highly linear viscosity data over a broad shear rate range – in this case, from $0.233 \bullet 10^6$ to $2.33 \bullet 10^6$ shear rate, at 150℃ with a 3.4 micron rotor-stator gap providing $1.0 \bullet 10^6 s^{-1}$ at 3500 RPM.

It was also of interest and significant value to apply the TBS to much higher shear rates and to a range of temperatures at which non-Newtonian calibration fluids were not available. This encouraged use of the inherent ability of the instrument to be applied as an absolute viscometer [32] where viscosity can be calculated from the values of the shear rate generated during operation and the shear stress measured by dimensions and physical calibration of the load cell.

ABSOLUTE VISCOMETRY – Use of the TBS as an absolute viscometer requires application of the elevator to change rotor position while operating the instrument to determine and then set the shear rate to that desired by using the reciprocal torque technique. This technique also permits easily changing shear rate or applying the desired shear rate to another temperature despite consequent unknown and significant changes of the very narrow rotor/stator gap with change of temperature.

The reciprocal torque technique utilized a simple variation of Newton's equation. At constant temperature, Equation 2 states that

$$\eta = cT/\dot{G}.$$

Since η and c are constants, then

$$T \propto \dot{G} \quad \text{(Eq. 3)}.$$

Changing the height of the tapered rotor, R_H, in the equivalently tapered stator proportionately changes the gap, g, between the rotor and stator, and

$$g \propto R_H \quad \text{(Eq. 4)}.$$

Since shear rate changes inversely with the gap between the rotor and stator,

$$g \propto 1/\dot{G} \quad \text{(Eq. 5)}.$$

Coalescing **Eq. 5, Eq. 3,** and **Eq. 4** results in:

$$R_H \propto 1/T \quad \text{(Eq. 6)}.$$

It is thus evident that by precisely and simply changing the tapered rotor height in the equivalently tapered stator at any given temperature, the height of the rotor is proportional to the reciprocal of torque. Consequently, with a set of different positions of the rotor and resultant torque values:

$$R_H = 1/T \cdot m + b \quad \text{(Eq. 7)}$$

in which **m** is the slope of the linear equation (and a measure of the instrument's torque sensitivity to viscosity) and **b** is the rotor depth at zero reciprocal torque.

However, the reciprocal of torque, $1/T$, has an interesting property. When $1/T$ is zero, torque, **T**, is infinite. The reasonable interpretation of this is that this position of the rotor is the theoretical contact between the rotor and the stator. The value of R_H at zero $1/T$ thus gives a reference position from which the rotor/stator gap can be calculated knowing their mutual taper as manufactured. (Obviously, actual contact of the rotor and stator should be carefully avoided.)

With this information and knowledge of the working taper of the rotor and stator, the proper rotor height for any shear rate can be set by simply determining the intercept of the reciprocal torque with a Newtonian fluid in **Equation 7** at whatever temperature is desired. Figures 9 and 10 show an example of this approach with a rotor and stator having a taper of 183/1.

In Figure 9, at 80°C the intercept of Newtonian reference oil R300 with the ordinate (Y-axis) occurs at a rotor height value of 13.779 mm. Intersection of the Newtonian R300 and the matching non-Newtonian


Fig. 9   Crossover Plot of Newtonian and Non-Newtonian Reference Oils at 80°C
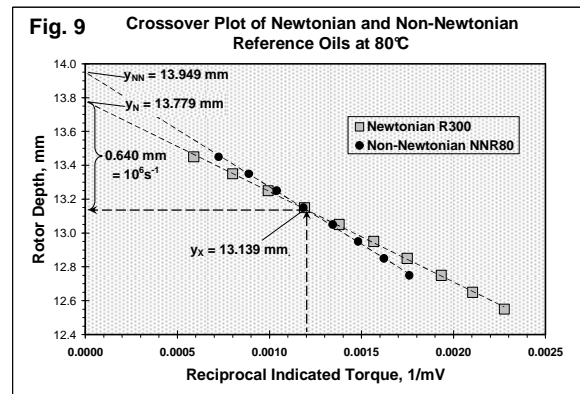
reference oil NNR-80 of equivalent viscosity, is at a rotor height of 13.139 mm for $1.0 \cdot 10^6 s^{-1}$ shear rate. The difference between the stator wall and the rotor position for this shear rate is calculated as $R_n = (13.779 - 13,139)$ mm = 0.640 mm. This difference between theoretical rotor contact with the stator wall and the intersection values can now be applied to establish the shear rate of $1.0 \cdot 10^6 s^{-1}$ at 40°C as in Figure 10.

Fig. 10   Plot of Newtonian Reference Oil at 40°C and Setting of Rotor Depth
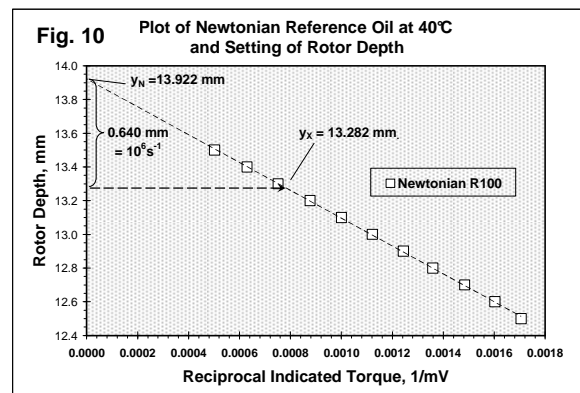
In Figure 10, at 40°C, the Newtonian reference oil intercepts the ordinate axis at a rotor height of 13.992 mm. Subtracting the known rotor height difference of 0.640 mm determined at 80°C as in Figure 9 gives a rotor position of $R_H = (13.992 - 0.640)$ mm = 13.282 mm to obtain a shear rate of $1.0 \cdot 10^6 s^{-1}$ for 40°C.

This procedure is now frequently used to precisely set the rotor/stator gap for the desired shear rate and then to apply this shear rate to determine the apparent viscosity of non-Newtonian fluids. In contrast, relative viscometers must always use non-Newtonian reference oils generated by absolute viscometry to establish the appropriate operating shear rate.

Acceptability of this technique is shown in Figure 11 in which the viscosities of the same reference oils were analyzed at both 80° and 40°C after setting the rot or height. It would be expected that with proper gap setting, the viscosity-torque values would fall on a straight line through the data and this is, in fact, the case. The intercept of the best line through the data with the ordinate (representing non-viscous, mechanical friction of the instrument) is essentially zero (less than 1% of the instrument's ~5500 mV torque range). The Coefficient of Determination, R^2, is good at 0.9987.

Fig. 11 Viscosity-Torque Correlation Comparison at 80℃ and 40℃ Using Four Newtonian Reference Oils
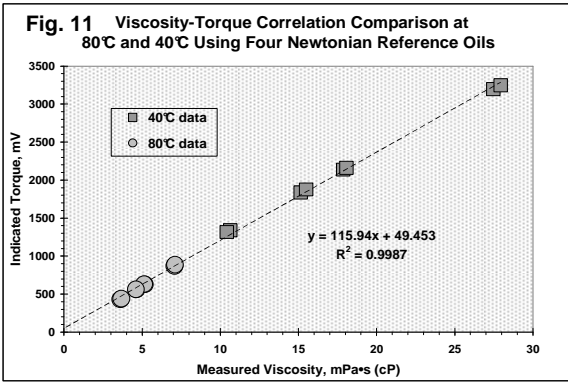
After a non-Newtonian reference oil is generated by absolute viscometry for a given temperature and shear rate, periodic use of this non-Newtonian oil provides a simple means of checking and, if necessary, slightly readjusting the rotor/stator gap by raising or lowering the tapered rotor. This, in turn, has permitted complete automation of the TBS (i.e. no operator attendance).

VERY HIGH SHEAR RATE STUDIES – In order to obtain very high shear rates, a combination of small rotor/stator gap and high rotor speeds is desired. Both of these conditions contribute to the generation of high shear rates. Moreover, the very narrow gap helps in reducing the heat generated since there is a smaller amount of fluid generating heat from viscous friction.

The absolute viscosity technique was used to develop the very high shear rate information shown in Figure 12 [33]. Rotor-stator gap was reduced to 0.78 microns and, at speeds of 800 to 6,000 RPM, the shear rate range was $1.0 \cdot 10^6$ to $7.5 \cdot 10^6 s^{-1}$. Even over this extended range, Newtonian behavior is evident from the best line through the data which gave $R^2 = 0.994$ with a Newtonian reference oil.

Fig. 12 Very High Shear Rate Newtonian Study
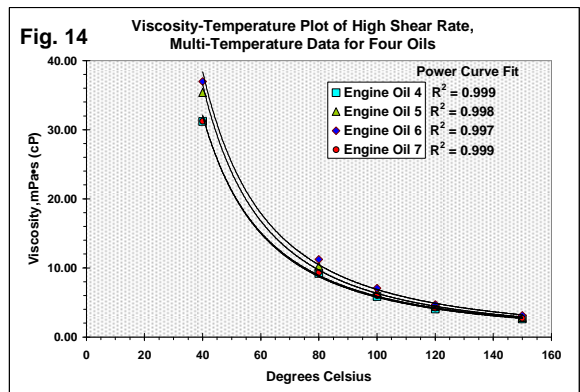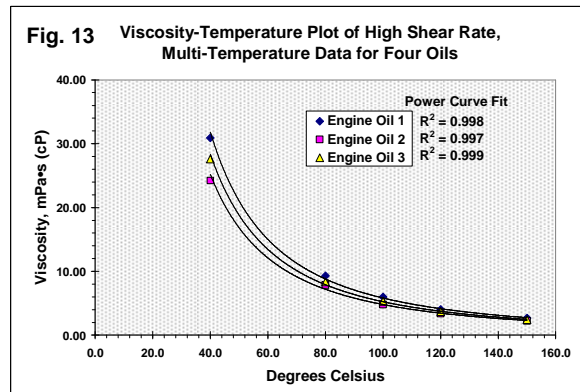1.0 million up to 7.5 million s^{-1} Shear Rate
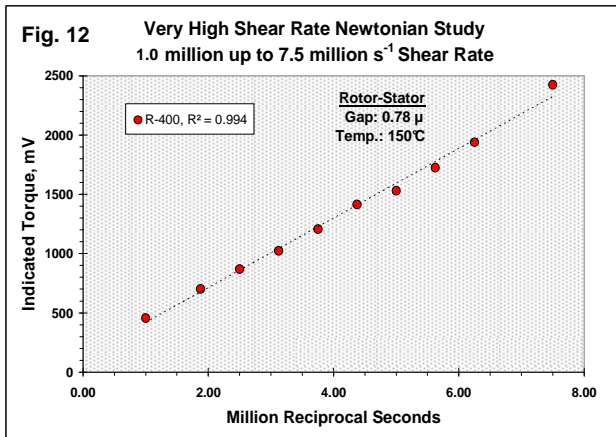
Since these studies were completed, the techniques developed for such very high shear rate viscometry have been successfully applied to a number of fresh and used engine oils, fuel-diluted engine oils, and hydraulic fluids to generate pertinent information. Success in such very high shear rate studies is, of course, directly related to the ability to control the temperature of the engine oil because of the very high fluid friction and resultant heat generation.

HIGH SHEAR RATE STUDIES AT LOWER TEMPERATURES – While the initial choice of 150℃ was helpful in the development of high shear rate rheology, there are also a number of lubrication sites in the engine that operate at lower temperatures, especially in starting and short trip driving effects. Recently, by applying advanced stator cooling techniques, studieswere made utilizing the instrument at high shear rates over a temperature range from 40° to 150℃.

The range of temperatures that seemed most appropriate for such study were 40°, 80°, 100°, 120 °, and 150℃. Since non-Newtonian calibration oils were available only at 80°, 100°, and 150℃, the instrum ent was applied in its capacity as an absolute viscometer to obtain viscosity values at 40° and 120℃.

Results of Lower Temperature Study – Seven engine oils were analyzed at the above five temperatures and $10^6 s^{-1}$ shear rate. Results are shown in Figures 13 and 14 for the exponential plots of viscosity versus temperature and, as listed in the graphs, these are well approximated by power curves with values of R² from 0.997 to 0.999.
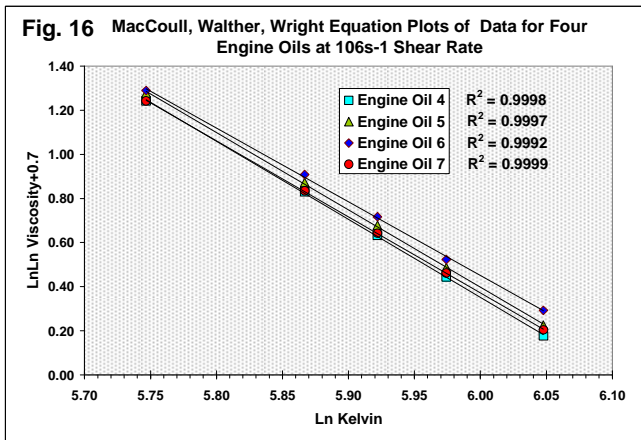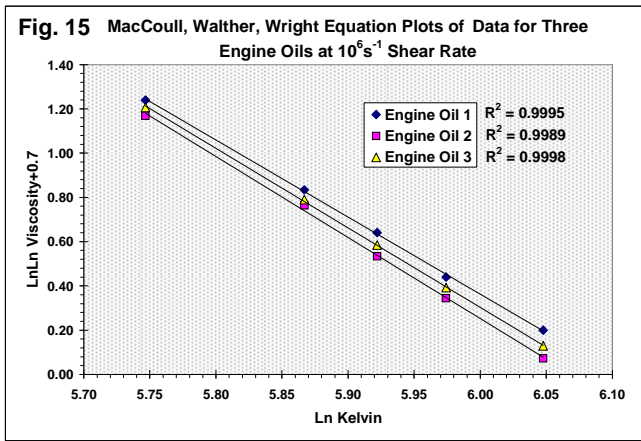
Perhaps of more interest, using the MacCoull, Walther,

Fig. 13 Viscosity-Temperature Plot of High Shear Rate, Multi-Temperature Data for Four Oils

Fig. 14 Viscosity-Temperature Plot of High Shear Rate, Multi-Temperature Data for Four Oils

Wright (MWW) relationship [33,34,35] developed for linearizing low shear rate viscosity data for purposes of interpolation (and, occasionally, extrapolation):

$$\text{Ln Ln } (\eta + 0.7) = \text{Ln K } m_2 + b \quad \text{[Eq. 8]}$$

(in which **K** is in degrees on the Kelvin scale, m_2 is slope and b_2 is intercept), it was found that high shear viscosity and temperature, also plot as straight lines as shown in Figures 15 and 16.

Fig. 15 MacCoull, Walther, Wright Equation Plots of Data for Three Engine Oils at $10^6 s^{-1}$ Shear Rate

Fig. 16 MacCoull, Walther, Wright Equation Plots of Data for Four Engine Oils at $10^6 s^{-1}$ Shear Rate

Use of Linear High Shear Rate Viscosity-Temperature Data – The fact that this high shear rate viscosity-temperature data gave linear MWW plots, suggests that the high shear rate data on engine oils can be interpolated (and perhaps extrapolated somewhat) over the range of temperatures studied. To the authors' knowledge, this is the first indication that the MWW viscosity-temperature relationship might be applicable to the high shear rate viscosity values of both Newtonian and non-Newtonian oils. This simplifies the generation of more such data at lower temperatures for those seeking high shear information over broad temperature ranges.

FORMS OF VISCOSITY LOSS – There are other areas in which high shear rate viscometry is useful and informative. One of these is coupled with low shear viscometry in generating the Viscosity Loss Profile (previously called the Viscosity Loss Trapezoid).

Polymers used as VI Improvers have two rheological responses to high shear stress (and rate) conditions called Temporary and Permanent Viscosity Losses.

Temporary Viscosity Loss – One response, discussed earlier in this paper called Temporary Viscosity Loss (TVL), is dependent on polymer configuration, solvency, polymer concentration, molecular weight (Mw), Mw distribution, and shear stress. High shear stress (rate) reflects the behavior of these VI Improvers under laminar flow as previously shown in Figure 5.

Permanent Viscosity Loss – The second response, also mentioned earlier, is caused by rupture of the polymer molecules and permanent loss of a portion of their viscous contribution to the fluid is also dependent on polymer configuration, concentration of polymer, and molecular weight, but reflects the effects of very intense levels of shear stress through various high energy processes such as cavitation of the solvating liquid. This response also results in viscosity loss but, because it reflects permanent reduction of the size and viscous contribution of the solvated macromolecules, it is termed 'Permanent Viscosity Loss' (PVL) usually expressed as %PVL.

Overall Viscosity Loss– Overall viscosity loss (OVL) is the difference between the fresh oil viscosity at low shear rate and the combined effects of PVL and the residual viscosity of the fluid at high shear rate after the fluid has been exposed to shear degradation of the dissolved polymer. This OVL value can be considered to reflect the viscosity of the used multi-grade engine oil in the operating engine if no other factors such as fuel dilution or oxidation are involved.

THE VISCOSITY LOSS PROFILE

Depending on their chemical composition, degree of solvation in the oil, concentrations, Mw, and Mw distributions, various VI Improvers respond differently to conditions producing both TVL and PVL. If the multi-grade oil is subjected to a degradation process, viscometric analyses at both low and high shear rates before and after degradation, produce four values. When the four viscosity values are plotted against shear rate [36], a trapezoid is produced as shown in Figure 17.


Fig. 17 - The Viscosity Loss Profile
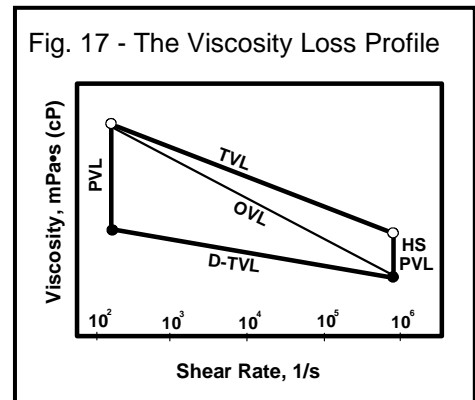
Five values are produced from the four viscometric measurements:
1. TVL
2. PVL
3. Degraded fluid TVL
4. Degraded fluid PVL
5. OVL

Different forms of trapezoids depend on the type of VI Improver [36]. Representations of two types of these profiles are shown in Figure 18 and indicate the ability of the VLP to distinguish VI Improver types as well as their effects on the rheological performance of various multi-grade oil in the operating engine.

Fig. 18 -- Viscosity Loss Profiles of two different types of VI Improvers
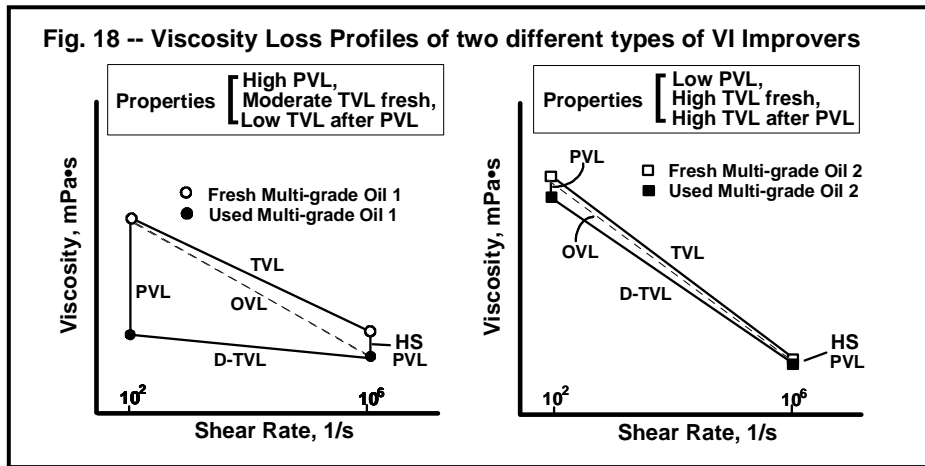
Moreover, the four values TVL, PVL, D-TVL, and D-PVL of each Profile also give information concerning the impact of the polymer degradation (rupture of the polymer chain) on the Mw distribution of the VI Improver before and after such exposure to cavitation [37]. This is related to the way in which the extended polymer coil responds to the severe distention and scission caused by cavitation and other highly energetic sources of polymer breakage.

The stress produced by cavitation tends to sever linear polymers at the site of greatest stress concentration – the midpoint of the macromolecule – and the molecular weight of the polymer undergoing chain scission is essentially halved. These shards of the original macromolecule are, of course, less distortable by the viscous 'grip' of the surrounding oil molecules and the fluid thus shows less TVL while their smaller size has less effect on viscosity.

Since control and reduction of both PVL and TVL is desirable, the Viscosity Loss Profile is a helpful tool in designing and choosing VI Improvers for various applications. High shear rate viscometry can be coupled with low shear rate viscometry to characterize the various polymers used to formulate multi-grade engine oils and other lubricants.

OBSERVATIONS AND DISCUSSION

The initial development of high shear rate viscometry in 1980 providing the ability to study and characterize the rheology of multi-grade engine oils has progressed considerably and led to an extended range of application both in shear rate and temperatures.

STANDARDS OF HIGH SHEAR VISCOMETRY – As a first principle, it is evident that suitably high standards of precision are as important in high shear rate instruments as in more commonly used, low shear rate viscometers. Any instrument used for high shear rate viscometry should be capable of 1) meeting Newton's criteria with a linear shear-rate/shear-stress ratio over the instrument's stated range of performance and 2) providing a sufficient level of precision and accuracy for reliable information.

Temperature Control – One of the most important factors in high shear viscometry at multiple, known values of shear rate is to be able to closely control operating temperatures of the test fluid. Otherwise, precision and accuracy of data are questionable.

Moreover, regarding shear rate dependent data of non-Newtonian fluids, it is desirable that the viscometer produce information at specifically determined shear rates (rather than averaged multiple shear rates) in order to clearly distinguish effects of changing shear rates and/or temperatures. In this respect, as mentioned earlier, rotational viscometry is the best instrumental tool.

Adjustable Tapered Rotor/Stator Geometry – Using the TBS, to obtain shear rates ranging from high to very high, the rotor/stator gap is adjusted to very small values – in the order of several microns to tenths of a micron. With a rotor diameter approximately one million times greater than the rotor/stator gap, rotor speeds varying by an order of magnitude (in the present case 800 to 8000 RPM) can produce these high to very high shear rates.

It is obviously necessary to know the absolute value of the gap between the rotor and stator in order to establish the shear rate and it is important to be able to easily and precisely adjust rotor position during operation of the viscometer without stopping rotation. By using a Newtonian fluid, and obtaining torque values at several rotor positions, the operating rotor/stator gap and the associated shear rate is determinable using the concept of the reciprocal torque intercept. Thus, with a known shear rate at any chosen temperature of viscometer operation, the apparent viscosities of non-Newtonian fluids can be determined at that temperature.

RECIPROCAL TORQUE INTERCEPT – The technique of using the reciprocal torque intercept is derived from Newton's equation and is essential in establishing the theoretical rotor-stator contact. From this and the known taper of the rotor/stator, a chosen shear rate can be set. Coupling this with the mechanically measurable values of torque, provides the values of shear rate and shear stress to use the TBS is an absolute viscometer, if desired.

The real value of the reciprocal torque intercept, however, is the ability to readily set the shear rate of the viscometer at different temperatures without a non-Newtonian reference oil available for that temperature.

VISCOSITY-TEMPERATURE LINEARITY OF HIGH SHEAR RATE VISCOMETRY – The finding reported in this paper that high shear rheology over a broad temperature range fits the was interesting and promising as a potential tool since this indicates that interpolation of such data may be made over a broad temperature range at a chosen shear rate.

The relationship was also somewhat surprising in that this is the first time that data have been reported showing that the linear MacCoull, Walther, Wright viscosity-temperature relationship developed for low shear kinematic viscometry in Stokes (Poise/density) also applies to high shear rate dynamic viscometry in Poise without regard to the degree of non-Newtonian response of a given oil at different temperatures.

Application of such data over a relatively wide range of operating engine temperatures and shear rates should provide insights into ways of improving fuel efficiency of modern engines concerning the most energy absorbing aspect of the engine – the engine oil. Some work has already been undertaken in this regard using the TBS at temperatures corresponding to those in various areas of the engine. This resulted in a Fuel Efficiency Index reported in the literature [38].

VISCOSITY LOSS PROFILE – There are other areas in which high shear rate viscometry is useful and informative. As mentioned, one of these applications is coupled with low shear viscometry in generating the Viscosity Loss Profile. As shown in Figure 18, Viscosity Loss Profiles (VLP) can differ markedly in appearance for different types of VI Improvers, and concentrations used in multi-grade oils. The VLP is also an effective tool in the development of VI Improvers and in appraising their performance in service.

SUMMARY

The studies presented in this paper give a view of the expanding range of precise high and very high shear rate viscometry. When applied, such information can add significantly to the present knowledge of rheology, lubrication, and energy management of lubricants and fluids

ACKNOWLEDGMENTS

BIBLIOGRAPHY

1. McMillan, M.L., "Engine Oil Viscosity Classifications – Past, Present, and Future", *SAE Symposium on the Relationship Between Engine Oil Viscosity and Engine Performance,* SP 416, *pp.21-31,* SAE, Warrendale, PA, 1977.

2. May, C.J., "A Brief History of the SAE Viscosity Classification System", *ASTM Symposium,* Lake Buena Vista, FL, Dec. 3, 2006.

3. Fenske, M.R., Klaus, E.E., and Dannenbrink, R.W., "Viscosity-Shear Behavior of Two Non-Newtonian Polymer-Blended Oils", *1950 ASTM Symposium on Methods of Measuring Viscosity at High Rates of Shear,* STP 111, ASTM, Philadelphia, PA, pp. 3-23, 1951.

4. Needs, S.J., "The Comparison of Viscosity-Shear Data Obtained with the Kingsbury Tapered Plug Viscometer and the PRL High Shear Capillary Viscometer", *ibid.,* STP 111, ASTM, Philadelphia, PA, pp. 24-44, 1951.

5. ASTM D02, Subcommittee 070B, Shear Stability of Multigraded Engine Oils, *DS 49 S-1,* ASTM, Philadelphia, PA, pp. 24-44, 1974.

6. West, J.P. and Selby, T.W., "The Effect of Engine Operation on the Viscometric Properties of Multigrade Engine Oils", *SAE Journal,* March, p. 42, SAE, Warrendale, PA, 1966.

7. Kuhn and Kuhn, *J. Colloid Science,* Vol. 3, p.11, 1948.

8. Peterlin, A., "Non-Newtonian Intrinsic Viscosity of Linear Macromolecules", *1960 ASTM Symposium on Non-Newtonian Viscometry,* STP 299, ASTM, Philadelphia, PA, 1962.

9. Philippoff, W., "Viscosity Measurements on Polymer Modified Oils", *ASLE Transactions,* Vol. 1, No. 1, pp. 82-86, Pergamon Press, N.Y., NY, 1958.

10. Brodnyan, J.G., Gaskins, F.H., and Philippoff, W., "Correlation between Rheological Parameters Measured in Instruments of Different Geometries", *ibid.,* STP 299, pp. 115-122, 1962.

11. Merrill, E.W., "Viscometry of Polymer Solutions in a Co-axial Cylinder Viscometer under High Rates of Shear", *ibid.,* STP 299, *ibid.,* pp. 73-84, 1962.

12. Selby, T.W., "The Non-Newtonian Characteristics of Lubricating Oils", *ASLE Transactions,* Vol. 1, No. 1, pp. 68-81, Pergamon Press, N.Y., NY, 1958.

13. Database on Engine Oils, published yearly by the Institute of Materials, Midland, MI, from 1984 to date.

14. Smith, M.F., "History of ASTM Involvement in High-Temperature, High-Shear Oil Viscosity Research", *ASTM Symposium on High-Temperature, High-Shear Oil Viscosity Measurement and Relationship to Engine*

Operation, ed. Spearot, J., ASTM STP 1068, pp. 3-13, ASTM, Philadelphia, PA, 1989.

15. Kingsbury, A., "Heat Effects in Lubricating Films", *Mechanical Engineering,* Vol. 55, pp. 685-688, 1933.

16. Barber, E.M., Muenger, J.R., and Villforth,Jr., F.J., "A High Rate of Shear Rotational Viscometer", *Annalen der Chemie,* Vol. 27, p. 425, 1955.

17. McMillan, M.L. and Murphy, C.K., "Temporary Viscosity Loss and its Relationship to Journal Bearing Performance", *1978 SAE Symposium on the Relationship between Engine Oil Viscosity and Engine Performance,* SP 429*,* pp.63-78, SAE, Warrendale, PA, 1978.

18. DuParquet, J., and Godet, A., "Assessment of Lubrication Conditions in a Big-End Bearing by Temperature Measurements – Correlation with High Shear Viscosity", *1977 SAE Symposium on the Relationship Between Engine Oil Viscosity and Engine Performance,* SP 434*,* pp.33-46, SAE, Warrendale, PA, 1979.

19. Pike, W.C., Banks, F.R., and Kulik, S., "A Simple High Shear Rate Viscometer – Aspects of Correlation with Engine Performance", *ibid.,* pp. 47-55, 1979.

20. Bondi, A., Physical Chemistry of Lubricating Oils, Reinhold Publishing, N.Y, NY, 1951.

21. Blok, H., C.R. Congress of Mechanical Applications, Paris, France, 1946.

22. Piasecki, D., Selby. T.W., and Smith, M.F., "Development and Performance of a Tapered Bearing Simulator for High Temperature, High Shear Viscometry", *SAE Paper #811225 (unpublished).*

23. Taylor, J.C., "The Ravenfield High Shear Viscometer", *Proceedings of the 1982 International Conference on the Viscometry of Automotive Lubricants,* pp. 25-36, Savant, Midland, MI, 1983.

24. Manning, R.E. and Lloyd, W.A., "Multicell High-Temperature, High-Shear Capillary Viscometer", *SAE Paper 861562*, SAE, Detroit, MI, 1986.

25. Multi-Instrument Round Robin, "Research Report for ASTM D4683, D4741, and D5181", conducted by ASTM Committee D02, Subcommittee 07, Section 0B, *ASTM Research Report D02-1378,* ASTM, Philadelphia, PA, 1996.

26. Kroepelin, H., Kolloid Zeitshrift, p. 294, 1929

27. ASTM D02 07 0B, The Relationship between High-Temperature Oil Rheology and Engine Operation – A Status Report, ASTM DS 62, ASTM, Philadelphia, PA, 1985.

28. Spearot, J.A., Ed., ASTM Symposium on High-Temperature, High-Shear Oil Viscosity Measurement and Relationship to Engine Operation, ASTM STP 1068. ASTM, Philadelphia, PA, 1989.

29. Newton, I., Philosophiae Naturales Principia Mathematica, Imprimatur: S. Pepys, Registered Society Praeses, 5 Julii, 1686. Revised and supplied with an historical and explanatory appendix by Cajori, F., edited by Crawford, R.T. (1934) and published by the University of California Press, Berkley and Los Angeles, 1966.

30. Miiller, G.C. and Selby, T.W., "Progress in Super-Shear Viscometry", *SAE 1996 Transactions, Journal of Fuels and Lubricants,* Section 4, pp. 869-876, SAE, Warrendale, PA, 1997.

31. Selby, T.W. and Tolton, T.J., "Very High Shear Rate, High Temperature Viscosity Using the Automated Tapered Bearing Simulator-Viscometer", *Proceedings of 7th International Colloquium Automotive Lubrication,* Technische Academie Esslingen, Ostfildern, Germany, 1990.

32. Selby, T.W. and Piasecki, D., "The Tapered Bearing Simulator – An Absolute Viscometer", *SAE Paper 830031,* 1983.

33. MacCoull, N., Lubrication, p.85, Texas Co., N.Y., NY, 1921.

34. Walther, C., Erdöl und Teer, Vol 4, p. 510, 1928.

35. Wright, W.A., "An Improved Viscosity-Temperature Chart for Hydrocarbons", *Journal of Materials,* Vol. 4, No. 1, p. 19, 1969.

36. Selby, T.W., "A Method of Generating and Appraising the Five Viscosity Loss Parameters of Lubricating Oils – The Viscosity Loss Trapezoid", *8th International Colloquium Tribology**, Proceeding Supplement, Section 4-4**,* pp. 1-14, Technische Acadamie Esslingen, Ostfildern, Germany, 1992.

37. Selby, T.W., "The Viscosity-Loss Trapezoid – Part 2: Determining General Features of VI Improver Molecular Weight Distribution Using Parameters of the Viscosity Loss Trapezoid", *SAE International Fuels and Lubricants Meeting and Exposition,* SAE Paper 932836, SAE, Warrendale, PA, 1993.

38. Selby, T.W., "The Viscosity-Dependent Fuel Efficiency Index for Engine Oils", *13th International Colloquium Tribology – Lubricants, Materials, and Lubrication Engineering**, Proceeding Supplement**,* pp. 35-39, Technische Academie Esslingen, Ostfildern, Germany, 2002.