

Rheology and oxidation of hydraulic fluid derived from bio-based material

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Petroleum oil has been the raw material for over 90% of hydraulic fluid. Limitations of this base material in the aspect of non-renewable, not environmental friendly and its sustainability in the future have prompted a search for more stable and environmentally friendly alternatives. This article presents rheological aspects of hydraulic fluid derived from bio-based material when used as hydraulic fluid. Palm oil with F10 additive was found to be most shear-stable. Various empirical models such as modified Power Law, Herschel-Bulkley and Arrhenius-type-relationship were used to evaluate the rheological data. The influences of shear rate and temperature on the variation of viscosity were clearly observed but temperature has more significant influence. Interpretations of rheological models indicate that crop oils belong to pseudo-plastic category. The effect of oil degradation in the aspect of physical property on viscosity was also evaluated.

I. INTRODUCTION

Biobased materials have emerged as promising alternatives to energy transport media because the material is a renewable resource and biodegrades quickly in soil. In contrast, most petroleum based and synthetic oils are produced from nonrenewable petroleum and do not degrade or degrade very slowly in soil. However, biobased materials do have some drawbacks. For example, biobased oil has poor oxidation stability and has non-Newtonian behavior.

The mineral oil is relatively cheap, has a wide viscosity range, compatible with various industrial components and machine and has been widely accepted fluid. This usage and advantages of mineral oil are known since the beginning of 80 century. However, in recent decades, people are more concerned on environment. This is due to the drawbacks of mineral oil which are high toxicity, in finite resource and has low biodegradability.

Considering the above disadvantages of mineral based lubricants, many biobased products have been produced and patented [1-3]. Consumers are looking for environmentally friendly and renewable products or bio base materials. Recent advances in the chemical additives and formulation techniques plus improved technology in product manufacturing have widened and diversified the field of application of vegetable oil to non-food applications.

The energy loss by shearing the lubricating oil is a function of material characteristics and operating conditions. The energy loss can be attributed to the oil

rheological properties [4]. The science of rheology has many influences in the field of oil flow and handling. Rheology concerns the flow and deformation of materials, in particular between the fluid and conduit. Moreover, rheology attempts to define a relationship between the stress acting on a given material and the resulting deformation and/or flow that takes place.

In this study, rheological behavior of vegetable oil with F10 and L135 commercial additives was investigated. Here we report generalized data on the rheological properties of palm oil-additive blends. Effect of oil degradation on oil rheological behavior is discussed.

II. RHEOLOGICAL MEASUREMENT AND ANALYSIS

A rotational viscometer (Brookfield DVIII), equipped with SP-18 spindle in a concentric cylindrical cup assembly was used for rheological measurement. The sample compartment was maintained at a constant temperature using a thermo container. The viscometer was calibrated with 4.7 cP Brookfield silicone viscosity standard. Three samples of oil were prepared: palm olein, palm olein with F10 and palm olein with L135. These oils were heated until 400 hours where oils sampling were conducted at 50, 150 and 400 hours. The viscosity of the oils was measured in duplicate at eight different shear rates range between 3 rpm and 100 rpm and temperature ranged from 40°C up to 100°C with an increment of 20°C. For each increment of 20°C, the oil

samples were left for 15 minutes until steady-state heat transfer was achieved.

The viscosity and percentage of torque were manually recorded when the viscosity reading reached apparent equilibrium (appears relatively constant for reasonable of time). The viscosities were calculated at eight different shear rates (3 rpm, 5 rpm, 6 rpm, 12 rpm, 20 rpm, 50 rpm, 60 rpm and 100 rpm) in mPa.s for each combination of vegetable oils and temperature. The shear rate and shear stress equations are shown below:

$$\gamma = 1.318 \times \text{Speed (rpm)} \quad (1)$$

$$\tau = 3.95 \times \text{Torque (\%)} \quad (2)$$

The shear rate dependence of the oil was investigated using the modified Power law and Herschel-Bulkley (Eqns. (3) and (5), respectively) of rheological models. The temperature dependence of the oil was investigated using the Arrhenius-type-relationship (Eqn. (4)). The experimental data were fitted to three models (shear rate dependence at 40, 60, 80, 100°C and temperature dependence at 3, 5, 6, 12, 20, 50, 60, 100 rpm). Below are the models:

$$\eta - (\eta_{\text{hrpm}} - \eta_{\text{ref}}) = K\gamma^{n-1} \quad (3)$$

$$\eta = \eta_{\infty, T} e^{\frac{E_a}{RT}} \quad (4)$$

$$\eta = K_H \gamma^{n_H-1} + \eta_{\infty, \gamma} \quad (5)$$

III. RESULTS AND DISCUSSIONS

Temperature is affecting the changes of viscosity. The influence of temperature on viscosity is even more significant than shear rate. From Fig. 1, it was found the viscosity of all vegetable oils approached low viscosity as the temperature increased. The increased of temperature tends to increase molecular motion (increase viscosity) and reduce attractive forces between molecules (reduce viscosity) [5,6]. In liquid, the reduced in attractive forces overcome the increased in molecular interchange and therefore viscosity reduces with increasing temperature.

It was found that the addition of additive (F10 and L135) has no improvement on the oil viscosity stability. For average percentage variation (include 50, 150 and 400 hours) of viscosity range between 40 and 100°C, olein has 75.3% (at 60 rpm) and 23.0% (at 3 rpm) of viscosity at 40°C. While, olein with F10 and olein with L135 exhibit more than 76.0% (at 60 rpm) and 23.0% (at 3 rpm) of viscosity at 40°C, over the same temperature range. Among all, pure olein alone has the highest

temperature stability behavior as temperature varies from 40 to 100°C.

The experimental data on the aspect of temperature were further elucidated through the use of model which was Arrhenius-type-relationship. Although the average percentage variation has been used to evaluate the experimental data but it is also equally important to further support the previously mentioned statement through model. From the model, the activation energy (E_a) estimated reflects the viscosity-temperature stability of the oil. Hence, oil with the smallest and highest values of E_a indicate the highly and lowly viscosity-temperature stability oil, respectively. Refer to Table I, results show that most of the pure olein E_a values smaller than olein with F10 and L135, at eight different speeds tested (3, 5, 6, 12, 20, 50, 60 and 100 rpm). Again, pure olein has outstanding viscosity-temperature stability.

At high shear rate, graphical evaluation on the effect of temperature shows that a continuous increase in temperature would reduce the viscosity variation of oils to a lower value. Therefore, by increasing the temperature it would modify the arrangement of oil molecular structure in a way that the effect of shear rate on the changes of viscosity would not be apparent. However, this effect is reversible as long as the increased of temperature do not create an optimal level to promote oxidation or degradation of oil molecular structure.

Instead of temperature, shear rate also play an important role in the variation of viscosity. Viscosity value reduces as shear rate increases, which is normally known as pseudo-plastic characteristic. As shear rate increases the reduction of viscosity was significantly observed, especially at the beginning of a very low shear rate. Continuously increase the shear rate would limit the effect of shear rate on viscosity where leveling off will be observed, refer to Fig. 2. Similar observation has been reported for the viscosity of waxy oils. This shear-thinning behavior is having flow behavior index (n) less than 1, refer to Table II. This behavior was observed as reversible and no time dependence while the shear applied breaks down the internal structure within the fluid very rapidly [7]. The highest flow behavior index value with n less than 1 indicates highly Newtonian behavior where shear rate has no influence on changes of viscosity.

It was found the viscosity of olein with F10 was less affected by shear rate compared to pure olein and olein with L135. This is supported by the fact that most of the flow behavior indexes of olein with F10 were greater than pure olein and olein with L135. In the aspect of average percentage variation of viscosity covered from 40 to 100°C between low (3 rpm) and high shear rate (60 rpm), it was found 60.3, 60.6 and 60.7 % of low shear rate (3 rpm) for olein with F10, olein with L135 and pure olein, respectively.

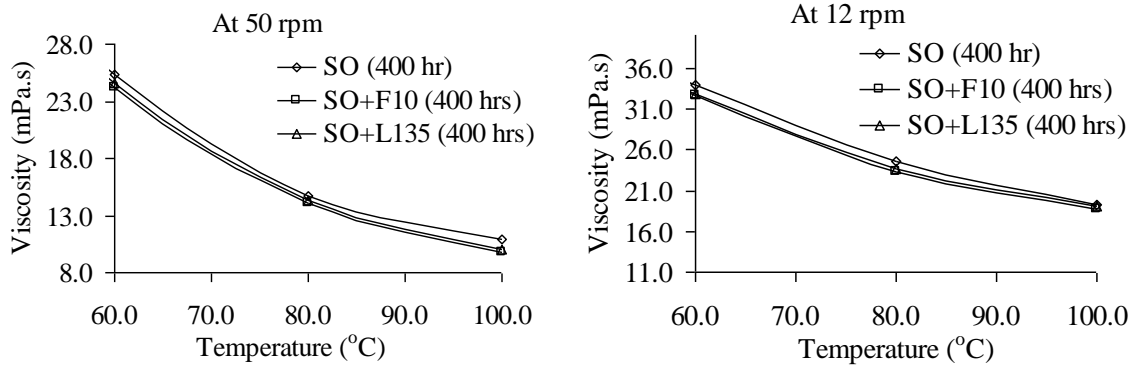


FIG. 1. The effect of temperature on viscosity at 50 and 12 rpm.

TABLE I. Different oils fitted by Arrhenius-type-relationship model and E_a values obtained.

Speed (rpm)	SO (hours)			SO +F10 (hours)			SO + L135 (hours)		
	50	150	400	50	150	400	50	150	400
100.0	23123	22216	22740	23420	22665	22471	23360	22283	22369
60.0	24256	22559	21960	24412	23093	23035	24400	22911	22873
50.0	23781	22381	22298	24109	22987	23372	24171	22839	23324
20.0	18759	17992	18679	18988	18449	19692	18651	18166	19399
12.0	14707	13596	13428	14296	13712	13581	13892	13674	13451
6.0	8232	7186	6637	9100	7366	6986	8836	7347	6822
5.0	8805	7300	6695	9144	7272	6786	9151	7295	6680
3.0	5245	4250	3697	5586	4397	3990	5514	4265	3883

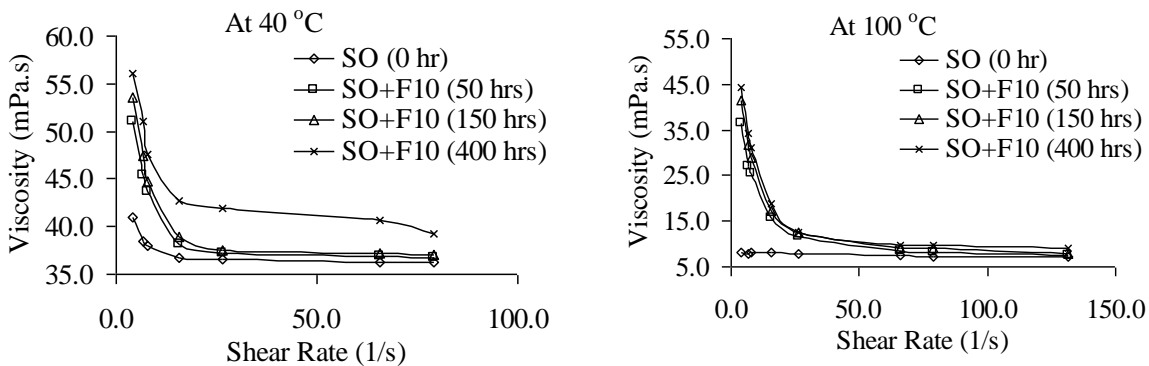


FIG. 2. The influence of shear rate on viscosity at 40 and 100°C.

By referring to shear rate dependence model, again it was found that most of the flow behavior indexes of olein with F10 were greater than pure olein and olein with L135 (refer to Table II). This indicates that olein with F10 exhibits the most Newtonian alike behavior. It also suggests that using olein with F10 as energy transport media would help to stabilize and minimize the shear-viscosity reduction effect.

For two viscosity-shear models fitted for different oils at different temperatures range from 40 to 100°C, the highest average correlation coefficient of 0.978 obtained by Herschel-Bulkley model and 0.953 for modified Power Law model. Theoretically, it is known that the consistency index indicates the level of oil viscous. Although the values of consistency index obtained from modified Power Law (K) and Herschel-Bulkley (K_H) for various oils (Tables III and IV) unable to provide a reliable observation on viscosity changes in the aspect of temperature, alternatively, graphical observation has already shown that viscosity dropped as temperature steadily increased (Fig. 3). Similar observation has been

reported for tomato pastes, edible oils and formate-based fluids [6,7].

The infinite-shear rate viscosities are also found to decrease as temperature increases (refer to Table V). The reduction in infinite-shear rate viscosity is important to be monitored closely since dramatic reduction in viscosity at this extreme condition could easily cause immediate failure to operating equipment.

The effects of heating time on the change of viscosity for olein, olein with F10 and olein with L135 were also studied. Results indicate that heating these oils from 0 to 400 hours could cause a permanent gradual increase in viscosity (refer to Fig. 4). This effect is only true for oils that shear at high shear rate: 60, 50 and 20 rpm. However, dramatic increase in viscosity was observed for oils sheared at 12, 6, 5 and 3 rpm. This phenomenon is significantly observed as the heating time reaches 50 hours for all oils tested and then, a leveling off was observed as the heating time continues. The increment of viscosity profiles due to heating can be characterized into two trends that is either power or exponential increase.

TABLE II. Different oils fitted by modified Power law model and n values obtained.

T (°C)	SO (hours)				SO +F10 (hours)			SO + L135 (hours)		
	0	50	150	400	50	150	400	50	150	400
40	0.879	0.634	0.598	0.648	0.653	0.608	0.653	0.643	0.603	0.650
60	0.941	0.511	0.518	0.546	0.469	0.513	0.538	0.459	0.513	0.539
80	0.949	0.481	0.485	0.481	0.500	0.485	0.486	0.492	0.486	0.479
100	0.980	0.532	0.499	0.479	0.542	0.504	0.471	0.539	0.498	0.469

TABLE III. Different oils fitted by modified Power law model and K values obtained.

T (°C)	SO (hours)				SO +F10 (hours)			SO + L135 (hours)		
	0	50	150	400	50	150	400	50	150	400
40	0.016	0.039	0.045	0.042	0.036	0.043	0.041	0.038	0.044	0.041
60	0.013	0.088	0.089	0.083	0.088	0.088	0.083	0.092	0.089	0.084
80	0.013	0.086	0.090	0.096	0.079	0.088	0.092	0.082	0.089	0.094
100	0.011	0.076	0.087	0.095	0.071	0.085	0.093	0.073	0.087	0.095

TABLE IV. Different oils fitted by Herschel-Bulkley model and K values obtained.

T (°C)	SO (hours)				SO +F10 (hours)			SO + L135 (hours)		
	0	50	150	400	50	150	400	50	150	400
40	0.036	0.068	0.079	0.062	0.070	0.079	0.061	0.073	0.078	0.062
60	-0.078	0.089	0.089	0.088	0.110	0.090	0.090	0.113	0.090	0.090
80	-0.045	0.111	0.107	0.104	0.107	0.107	0.102	0.108	0.107	0.104
100	0.143	0.089	0.105	0.113	0.089	0.102	0.111	0.089	0.105	0.111

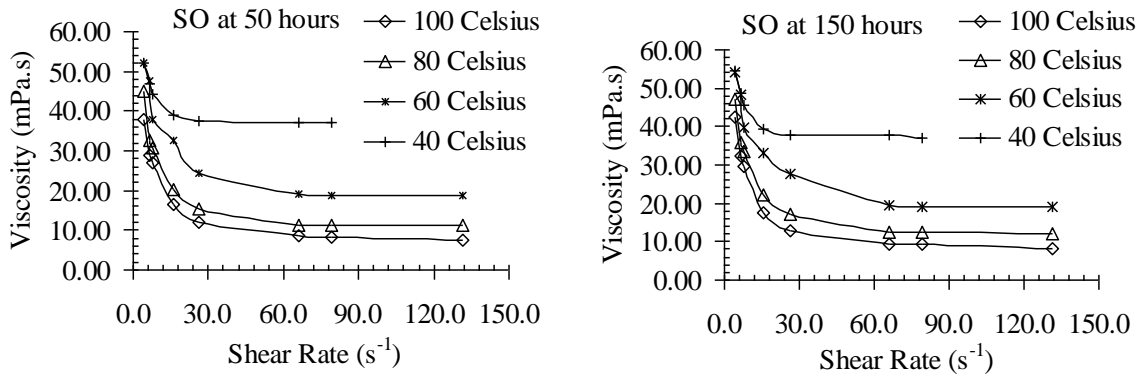


FIG. 3. The influence of shear rate on viscosity at different temperatures.

TABLE V. Different oils fitted by Herschel-Bulkley model and $\eta_{\infty,\gamma}$ values obtained.

T (°C)	SO (hours)			SO +F10 (hours)			SO + L135 (hours)		
	50	150	400	50	150	400	50	150	400
40	0.0357	0.0360	0.0392	0.0358	0.0359	0.0385	0.0359	0.0358	0.0388
60	0.0101	0.0084	0.0160	0.0146	0.0108	0.0163	0.0144	0.0100	0.0165
80	0.0079	0.0078	0.0076	0.0083	0.0078	0.0076	0.0080	0.0078	0.0077
100	0.0038	0.0043	0.0053	0.0044	0.0040	0.0047	0.0042	0.0043	0.0047

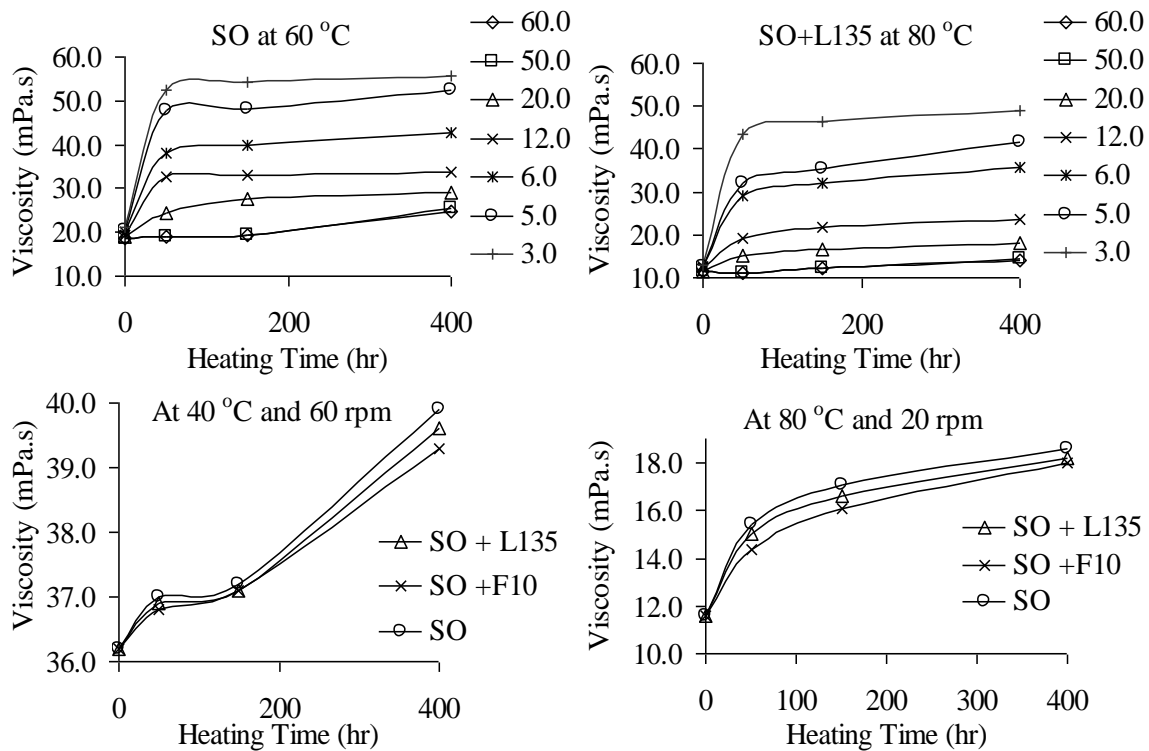


FIG. 4. The influence of heating time on viscosity.

IV. CONCLUSIONS

The effects of shear rate and temperature on the reduction of viscosity are obvious. However, shear rate has less effect on viscosity compared to the influence of temperature. In short, oxidation has some effect on the material rheological behavior. All oils tested behave towards pseudo-plastic category where olein with additive F10 is behaving more to non-pseudo-plastic characteristic while pure olein and olein with L135 are experiencing pseudo-plastic alike behavior. From the interpretation of rheological models and average percentage variation observation, it is conclusive that pure olein is highly viscosity-temperature stable while olein with F10 shows Newtonian characteristic and less is viscosity-temperature stable. These viscosity-shear rate and viscosity-temperature profiles are important to be monitored closely since reduction in oil viscosity could easily cause thinner lubricant film or less lubricant film strength and also failure to the energy transport media or bio-energy media. This will result in higher internal friction on operating equipment and will eventually reduce the operating life of fluid and also the service life of equipment. Olein with F10 which shows strong Newtonian behavior and has lowest gel strength promises possible application as bio-energy media with variations in agitation or shear during start-up thus promoting less friction. Although this is an initial stage of viscosity improvement by direct blends of additives, an in-depth study, vegetable oils structure with proper chemistry modification could produce products for lubricants, fuels and additives applications.

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NOMENCLATURES

E_a activation energy, N.m.mol⁻¹
 K, K_H consistency index, mPa.sⁿ

n, n_H flow behavior index, dimensionless
 R universal gas constant, N.m.K⁻¹.mol⁻¹
 T temperature in Kelvin, K
 τ shear stress, kg.m⁻¹.s⁻²
 τ_g gel strength, kg.m⁻¹.s⁻²
 γ shear rate, s⁻¹
 $\eta, \eta_{hrpm}, \eta_{ref}, \eta_{\infty,T}, \eta_{\infty,\gamma}$ viscosity, viscosity at the highest round per minute, focus point of all curve lines (0.010 Pa.s), viscosity at infinite-temperature, infinite-shear rate, Pa.s

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