

HIGH PRESSURE TRIBOLOGICAL BEHAVIOR OF VEGETABLE OILS AS LUBRICANT

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ABSTRACT

Vegetable oils as base oil for lubricants are environmentally preferable to mineral oils. They are usually excellent boundary lubricants but their high-pressure behavior is not investigated yet properly. In this research, authors measured some high-pressure tribological properties of vegetable oil and compared its effect on lubrication. It is well known that the high-pressure tribological properties of oils are important for the traction control and the prevention of surface failure under elastohydrodynamic condition. Viscosity-pressure-temperature relation and density-pressure-temperature relation are important to know the performance of lubricant at high-pressure condition. Vegetable oils showed high viscosity index, whereas low-temperature characteristics are not sufficiently good. High content of wax has shown the effect on the bulk modulus and the solidification temperature of vegetable oils. Moreover, vegetable oils showed sufficiently good properties at temperature of 40 to 60 °C. It would be the alternate of some mineral oils.

Keywords: Vegetable oil, Viscosity, Density.

1. INTRODUCTION

It is well known that mechanical systems often employ lubricants, the majority of which are petroleum based, to decrease component friction and surfaces wear. Now a days, due to rising of petroleum based oil prices, the diminishing supplies of natural resources, global climate change and increased environmental sensitivity, various alternatives to petroleum based lubricants are currently being explored. Such alternatives include synthetic lubricants and vegetable based lubricants. Oils and fats of vegetable and animal origin were extensively used as lubricants till the middle of the 19th century. In general, vegetable oils are highly attractive substitutes for petroleum based oils because they are environmentally friendly, renewable, less toxic and readily biodegradable.

Vegetable oils exhibit positive production trends and show good potential for a variety of industrial applications. The worldwide production of oilseed is increasing day by day, but at present it is costly compared to petroleum based oils. Economic losses are justified when considering the life cycle advantages of vegetable based lubricants [1]. From both production and life cycle standpoints, the future seems optimistic for vegetable oils as a viable replacement for petroleum based lubricants.

In general, when compared with mineral oil base stokes, vegetables oils have the following advantages: higher viscosity index, lower evaporation loss and enhanced lubricity, which leads to improved energy

efficiency. However, vegetable oils have performance limitations, particularly in thermal, oxidative and hydrolytic stability [2]. Vegetable oils typically contain about 80-95% fatty acids, which are one of the main performance improvers in lubricants [3]. On the other hand, mineral oil typically contains saturated aliphatic compounds, namely paraffinic and naphthenic, and small amount of aromatics. Thereby, mineral oils are more stable than vegetable oils through their chemical nature, but they have poorer lubricity [4].

Vegetable oils are usually excellent boundary lubricants but their high-pressure behavior is not investigated yet properly. In this research, authors measured some high-pressure tribological properties of vegetable oils and compared its effect on lubrication. It is well known that the high-pressure tribological properties of oils are important for the traction control and the prevention of surface failure under elastohydrodynamic condition [5]. Viscosity-pressure-temperature relation and density-pressure-temperature relation are important to know the performance of lubricating oil at high-pressure condition. Among the vegetable oils castor oil, olive oil, rapeseed oil, camellia oil, mustard oil and coconut oil are considered as testing lubricating oil.

Vegetable oils showed high viscosity index, which is an important property of lubricant. Whereas low temperature characteristics are not sufficiently good as mineral oil, especially coconut oil showed highest solidification temperature. Solidification temperature at atmospheric pressure was measured by low temperature

test using liquid nitrogen. Pressure-viscosity coefficient α of these oils has measured by measuring the viscosity at various pressures. Density at various pressures was measured by high-pressure densitometer at different temperature. Comparing all the results, vegetable oils showed sufficiently good properties at temperature of 40 to 60 °C. It can be used in elastohydrodynamic lubrication due to remarkable pressure-viscosity coefficient. Vegetable oils would be the alternate of mineral oil.

2. SAMPLE OIL

Six kinds of vegetable oil were tested. The list of tested oils and their physical properties are given in Table 1, where ρ is density in g/cm^3 ; ν is kinematic viscosity in mm^2/s .

Table 1: Physical properties of tested oils

Oil name	Density	Kinematic Viscosity ν		Viscosity Index
	ρ	Viscosity ν		
	(g/cm^3)	(mm^2/s)	(mm^2/s)	
	15°C	40°C	100°C	
Castor oil	0.9666	241.0	17.5	75
Olive oil	0.9137	39.6	8.2	190
Rapeseed oil	0.9456	39.1	8.3	196
Camellia oil	0.9168	39.3	8.3	194
Mustard oil	0.9180	44.1	9.4	205
Coconut oil	0.9260	27.6	5.9	165
Mineral oil (P150)	0.8663	28.6	5.1	105

3. CHEMICAL STRUCTURE

The chemical structure of vegetable oils is relatively uniform, as opposed to mineral oil. Nearly all necessary fundamental information on vegetable oils can be found in the hand book of oil chemistry [6]. Triglycerides are the main constituents of vegetable oils. They are fatty acid esters of glycerol. The fatty acids (mainly straight chain C_8 through C_{24} with or without double bonds) can be classified into saturated, monounsaturated, polyunsaturated and specialty (hydroxy, epoxy, etc.). Molecular weight of the Triglycerides is around 900 amu. Obviously, the differences in chemical structure from mineral oils are very significant.

The fatty acid composition in weight percentage of vegetable oils is given in Table 2. Among the fatty acids caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid and stearic acid are the saturated fatty acid. Whereas oleic acid, ricinoleic acid, gadoleic acid and erucic acid are the monounsaturated fatty acid but linoleic acid and linolenic acid are polyunsaturated fatty acid. In the tested vegetable oils, coconut oil has the higher content of saturated fatty acids and castor oil has mainly ricinoleic acid, which can be classified as hydroxy monounsaturated fatty acid. Rapeseed oil and mustard oil are almost same type of oil, here mustard oil was collected from directly pressed mustard seeds, which shown a little bit different chemical composition at higher carbon series.

Table 2: Fatty acid composition of vegetable oils

Fatty acid	Castor oil	Olive oil	Rapeseed oil	Camellia oil	Mustard oil	Coconut oil
C_8 Caprylic	-	-	-	-	-	7.7
C_{10} Capric	-	-	-	-	-	6.2
C_{12} Lauric	-	-	-	-	-	47.0
C_{14} Myristic	-	-	-	-	-	18.0
C_{16} Palmitic	1.1	9.8	3.9	8.2	3.5	9.5
C_{18} Stearic	1.0	3.2	1.8	2.1	1.6	2.9
$\text{C}_{18:1}$ Oleic	4.1	73.8	57.9	85	19.7	6.9
$\text{C}_{18:1}+\text{H}$ Ricinoleic	88	-	-	-	-	-
$\text{C}_{18:2}$ Linoleic	4.8	11.1	21.8	4.1	22.2	0.2
$\text{C}_{18:3}$ Linolenic	0.5	0.4	11.3	0.6	13.4	-
$\text{C}_{20:1}$ Gadoleic	-	-	1.7	-	13.8	-
$\text{C}_{22:1}$ Erucic	-	-	1.0	-	21.4	-
Other	0.7	1.7	2.3	-	4.4	1.6

4. EXPERIMENTAL DETAILS

4.1 Solidification Temperature at Atmospheric Pressure

When a minute air bubble is closed into a space between test fluid and a cover glass plate, its volume apparently expands as a result of contraction of the fluid by cooling. Thus expanded bubble generates tensile stress along its interface under solidified condition. At the same time the photoelastic effect appears under a dark polarized field. Due to high content of wax in vegetable oils (since vegetable oil contains of triglyceride fatty acids), the detection of initial appearance of the photoelastic effect is difficult. For the vegetable oils dark field observed throughout the bubble and liquid oil due to its solidification. Solidification temperature at atmospheric pressure T_{S0} was measured observing that phenomena by lowering the temperature using liquid nitrogen [7]. Among the vegetable oils, coconut oils showed the highest solidification temperature. The solidification temperature at atmospheric pressure of castor oil, olive oil, rapeseed oil, camellia oil, mustard oil and coconut oil is -58 , -14 , -26 , -27 , -26 and $+7$ °C respectively.

4.2 High-Pressure Viscosity Measurement

A high-pressure falling ball viscometer is used to determine high-pressure viscosity up to 0.4 GPa and at temperature from 20 to 60 °C in the range of viscosity $\eta < 10^3$ Pas, where η is the absolute viscosity. The schematic diagram of the high-pressure falling ball viscometer is shown in Fig.1. The basic principle is that a solid body having higher density than the liquid to be tested slowly falls through a liquid filled tube. The density difference and the gap between the falling body and the tube wall determine the viscosity of the falling body. High-pressure viscosity of castor oil was measured at 20 to 100 °C but coconut oil was measured at 40 and 60 °C temperature. The viscosity pressure relation at 40 °C temperature is shown in Fig 3.

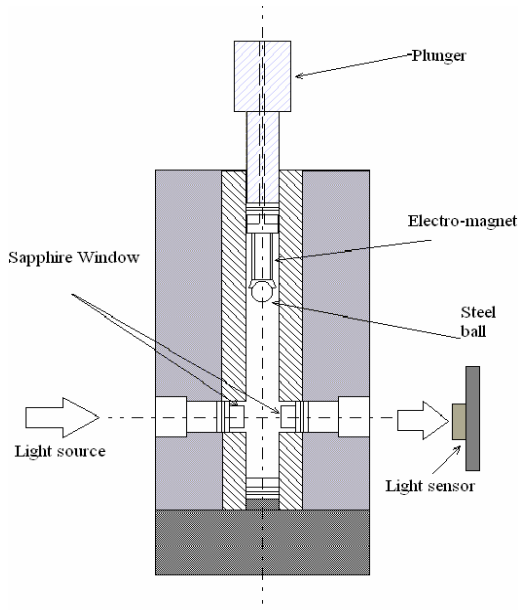


Fig 1: High pressure falling ball viscometer

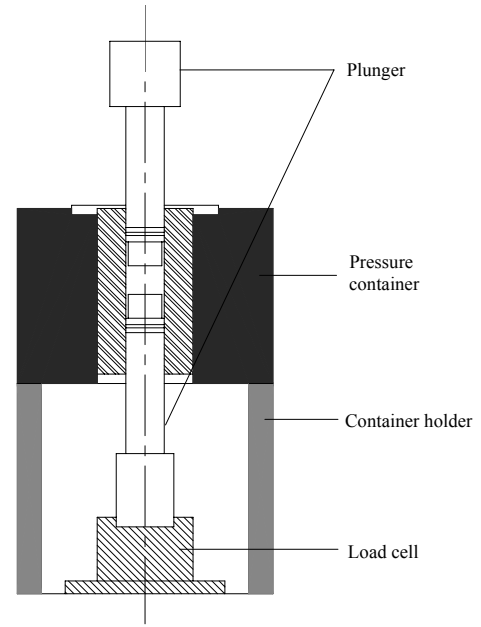


Fig 2: High-pressure densitometer

4.3 High-Pressure Density Measurement

The high-pressure density measurement of the test fluids was done by the high-pressure densitometer shown in Fig 2. The test fluid of 2 mL was poured into the test machine and pressure was applied in the upper plunger by a hydraulic power unit. The density was determined corresponding to pressure by measuring the fluid volume in the machine by linear gauge. The isothermal compressibility influence was considered in the experiment.

One of the basic equations for the solidification of oils is the equation of volumetric change, which is used in the strength of materials [8]. The volumetric strain ε is defined as the ratio of decrease in volume to the original volume:

$$\begin{aligned} \varepsilon &= \frac{dV}{V} \\ &= \left(-\frac{\partial \ln \rho}{\partial p} \right)_T dp + \left(-\frac{\partial \ln p}{\partial T} \right)_p dT \\ &= \left(-\frac{1}{K} \right) dp + 3\delta dT \end{aligned} \quad (1)$$

where V is the volume, ρ is the density, p is the pressure, T is the temperature, K is tangent bulk modulus and δ is coefficient of thermal expansion.

5. RESULTS AND DISCUSSION

Vegetable oils showed high viscosity index, which is an essential property of lubricating oil. The kinematic viscosities of vegetable oils are shown in Table 1. Except castor oil, the viscosities at 100 °C are very close to meeting SAE30 grade requirements and at 40 °C they are in between the ISO 32 and ISO 46 viscosity grades. However, the viscosity of castor oil is significantly

higher and it falls into the upper region of the ISO VG 220 specification at 40 °C. The presence of the hydroxy group in ricinoleic acid, the main component of castor oil, induces stronger hydrogen bonding among the triglyceride molecules, causing the intermolecular attraction forces to become much more intense. At 100 °C the kinematic viscosity of castor oil falls into the upper region of the viscosity requirements for an SAE 90 gear oil specification. The viscosity index (VI) of castor oil is higher when compared to most mineral oils (but here less than the compared mineral oil P150N) but is much lower than conventional vegetable oils. This can be explained by the fact that hydrogen bonding becomes less substantial with increasing temperature. The effect of viscosities continued on the high-pressure.

Viscosity at various pressures was measured for all tested vegetable oils. The change of absolute viscosity with respect to pressure at temperature of 40 °C is shown in Fig 3. From the graph, using Barus's equation pressure viscosity coefficient α was calculated. The value of α for all vegetable oils at 40 °C is given in Table 3.

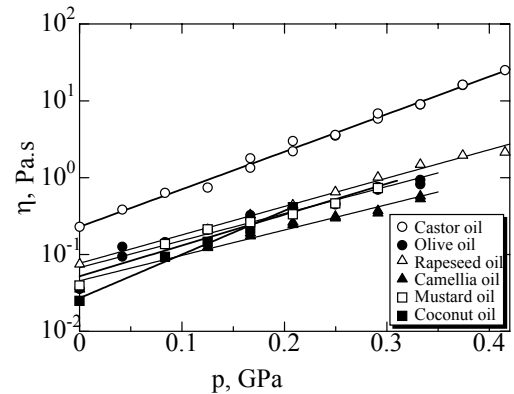


Fig 3: Viscosity-pressure relation at 40 °C temperature

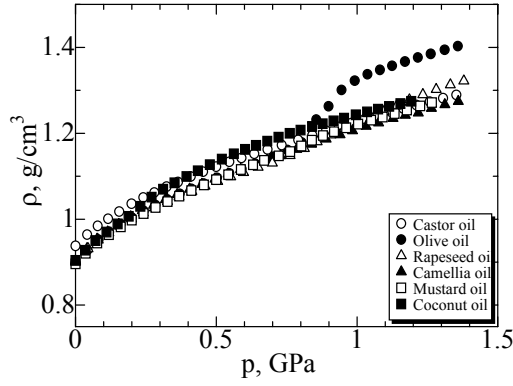


Fig 4: Changes of density with pressure

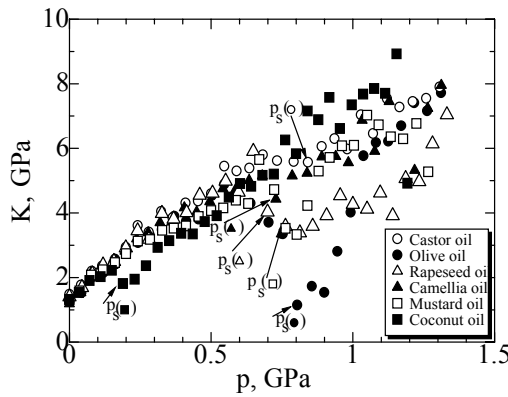


Fig 5: Tangent bulk modulus and pressure relation

Pressure-viscosity coefficient α of vegetable oils has found comparatively lower value than the mineral oil. Due to high content of saturated fatty acid, coconut oil has shown the higher pressure-viscosity coefficient, which is comparable with the mineral oil. The variation of pressure-viscosity coefficient α with temperature can also be described by

$$\alpha = C_1 + C_2 \log_{10} \nu \quad (2)$$

where ν is kinematic viscosity (mm^2/s), C_1 and C_2 are the parameters depend on oils properties. The parameters C_1 and C_2 for the tested oils are given in Table 3. High-pressure viscosity can also be predicted by Ohno's viscosity-pressure-temperature correlation [9].

Table 3: Parameters for the pressure-viscosity coefficient

Oil name	α at 40 °C (GPa^{-1})	C_1 (GPa^{-1})	C_2 (GPa^{-1})
Castor oil	11.25	2.107	1.657
Olive oil	8.10	1.706	1.738
Rapeseed oil	9.35	3.772	1.589
Camellia oil	6.96	-4.519	3.126
Mustard oil	9.46	5.947	1.061
Coconut oil	13.09	0.888	3.680

Density of vegetable oils at atmospheric pressure is higher than the compared mineral oil. The change in density ρ against pressure of vegetable oils at 40 °C temperature is shown in Fig 4. The tangent bulk modulus $K = (\partial \ln \rho / \partial p)^{-1}$ was found by differentiating the density-pressure curve shown in Fig 5. The solidification point is obvious from the abrupt change of dK/dp in the figure. Due to high contents of wax in vegetable oils, abrupt change of bulk modulus was found at high pressure. Among the vegetable oils, olive oil has shown the different behavior in Fig 4 and Fig 5 due to high content of oleic acid in olive oil. Solidification point of mustard oil and coconut oil at 40 °C temperature has found as 0.762 GPa and 0.189 GPa correspondingly. Solidification points of other oils can also be found on the same way.

The phase diagram of castor oil, mustard oil and coconut oil is shown in Fig 6. The diagram was drawn up to temperature of 60°C. For the higher temperature and pressure phase behave can found by Diamond Anvil Cell (DAC) experiment [10]. The equation related to the temperature-pressure of solidification point T_s is represented in the following empirical formula as Eq. (3).

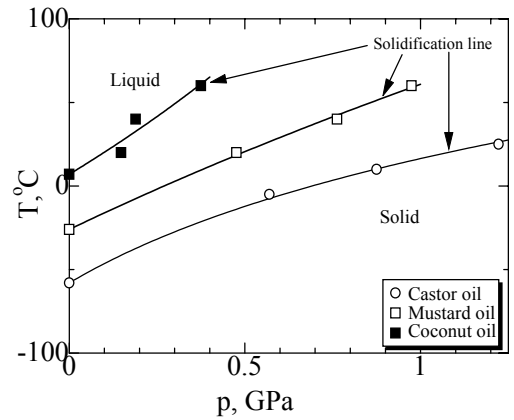


Fig 6: Phase diagram of castor, mustard and coconut oil

$$T_s = T_{s0} + A_1 \ln(1 + A_2 p) \quad (3)$$

where A_1 and A_2 are the parameters which depend on oil properties. The parameters with solidification temperature at atmospheric pressure T_{s0} are given in Table 4.

Table 4: Parameters for the solidification equation

Oil name	T_{s0} (°C)	A_1 (°C)	A_2 (GPa^{-1})
Castor oil	-58	77.77	1.605
Mustard oil	-26	308.76	0.327
Coconut oil	7	-117.58	-1.014

The phase diagram also depends on the chemical composition of the oil. Here, the fatty acid composition has the impact on the phase behavior of vegetable oils.

Since coconut oil has a huge amount of lauric acid and other saturated fatty acids, it showed the phase behavior as shown in Fig 6 in the top of the figure. The phase behavior of castor oil is also shown in the figure at the bottom position comparing other two vegetable oils. The difference in lubricant performance of castor oil may be due to its chemical composition. Castor oil is the only vegetable oil with such a high content of hydroxy fatty acids as ricinoleic acid [11].

6. CONCLUSIONS

In this research, high-pressure viscosity, high-pressure density, pressure-viscosity coefficient, solidification point and phase behavior were pointed out by corresponding experiments. Vegetable oils are good in boundary lubrication and environmentally preferable to mineral oil. The outcome of the experiments are summarized as:

- (1) Vegetable oils showed high viscosity index and viscosity is good compared to mineral oil at atmospheric pressure and also moderate high pressure.
- (2) Pressure-viscosity coefficient of vegetable oils showed lower values compared with mineral oil and due to low pressure-viscosity coefficient, these can be used in EHL at moderate high-pressure.
- (3) The increment of density with pressure of vegetable oils is also sound good. Olive oil has high content of oleic acid and showed different behavior as like ionic oil.
- (4) Due to high content of wax in vegetable oils, the abrupt change of bulk modulus has found at high pressure. That indicated the change of phase of the vegetable oils at corresponding temperature.
- (5) Phase behavior has found and it has showed the phase diagram of castor oil, mustard oil and coconut oil. The highest solidification temperature has found for coconut oil. The solidification pressure of mustard and coconut oil at 40 °C temperature has found as 0.762 GPa and 0.189 GPa respectively, others are also shown in tangent bulk modulus and pressure relation.

7. REFERENCES

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8. NOMENCLATURE

Symbol	Meaning	Unit
α	Pressure-viscosity coefficient	(GPa ⁻¹)
η	Absolute viscosity	(Pa.s)
ν	Kinematic viscosity	(mm ² /s)
ρ	Density	(g/cm ³)
K	Tangent bulk modulus	(GPa)
A ₁	Constant	(°C)
A ₂	Constant	(GPa ⁻¹)
p	pressure	(GPa)
T	Temperature	(°C)
T ₅₀	Solidification temperature at atmospheric pressure	(°C)
T _s	Solidification temperature at any pressure p	(°C)