

Analysis of Viscosity-Temperature Behaviour of Karanja Oil Trimethylolpropane Ester Bio-lubricant Base Stock

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The work presented deals with the viscous flow characterization of karanja oil based bio-lubricant base stock. Karanja oil trimethylolpropane ester (KOTMPE) bio-lubricant base stock was prepared from karanja oil methyl ester (KOME) and trimethylolpropane (TMP) using acid-catalyzed transesterification synthesis protocol. The viscosities were measured at 10-60 °C and 10-1000 s⁻¹ shear rates using model HR-3 Discovery Hybrid rheometer. The viscosity-temperature interdependences at different shear rates were modeled using the Arrhenius equation. The viscosity values predicted with Arrhenius model were found in good agreement with measured values. The flow behaviour index of KOTMPE bio-lubricant stretched from 1.036 to 1.527, which suggested a gradual shift in fluid behaviour from Newtonian to non-Newtonian with increase in temperature. The study confirmed that Arrhenius equation along with Ostwald-deWaele power law could be used to predict the apparent viscosity and flow behaviour of synthesized KOTMPE bio-lubricant oil.

Keywords: Karanja oil, Ester, Arrhenius equation, Ostwald-deWaele power law, Flow behaviour index, Activation energy.

INTRODUCTION

The world annual lubricating oil production stands around 40 million metric tons [1], of which about 50 % is lost to the environment [2,3]. In recent years, vegetable oils based bio-lubricants have emerged as a potential substitute for mineral oil based lubricants on account of their superior environment friendly and lubricity characteristics [4].

Almost all vegetable oils (edible and non-edible) have been worked upon by researchers for application as lubricants with varying degrees of success. These oils may be used without any chemical modification or may be blended with petroleum lube oil base stocks or additives or may be chemically modified *via* esterification, transesterification, epoxidation and hydrolysis routes. The major vegetable oils analyzed for bio-lubricant applications include castor oil [5], canola oil [6], soybean oil [7], sunflower oil [8], palm oil [9], *Jatropha curcas* oil [10], rapeseed oil [11], rubber seed oil [12], *etc.* Since the edible vegetable oils are more important for human civilization as key source of nutrition, the bio-lubricant research has gradually shifted to non-edible vegetable oils such as karanja, linseed, tobacco, waste cooking oil [13], algae oil and microalgae [14] and animal fats.

Rheology is the study of flow and deformation of material under application of stress [15]. The rheological behaviour of a material is thus a relationship between stress and deformation appropriately represented by a mathematical expression consisting of the necessary variables and a few constants. These constants are characteristic for a given material [16]. In general, the need for rheological study of a material appears from the assumption that measured rheological behaviour may prove of considerable significance to material characterization, quality control, process control and modeling in industrial situations [17,18]. The precise knowledge of the rheological properties of karanja oil (KO), karanja oil methyl ester (KOME) and karanja oil trimethylolpropane ester (KOTMPE) is essential in movement of bulk quantities of these oils to have better control over oil velocity, pump pressure and energy requirement in esterification and transesterification process steps [19].

The rheological characteristics of mineral and renewable ecological bio-lubricants have been analyzed at wide ranges of temperature and shear rate parameters by researchers. Arrhenius equation has been applied by most researchers to express the effect of temperature on apparent viscosity of test oils. Sathivel *et al.* [20] studied the rheological properties of unrefined pollock oil at different temperatures at shear rates varying from

0 to 500 s⁻¹ using AR2000 rheometer fitted with a cone plate geometry. In similar manner, Huang and Sathivel [19] studied the rheological properties of unpurified salmon oil at 5, 10, 15, 20, 25, 30 and 35 °C and shear rates varying from 0 to 500 s⁻¹ using advanced AR2000 TA Instruments rheometer. The temperature and the apparent viscosity of oil were fairly correlated through the given Arrhenius relationship: $\mu = A \exp(E_a/RT)$. Quinchia *et al.* [21] studied the low temperature viscous flow behaviour of castor, rapeseed, soybean, sunflower and high oleic sunflower oils blended with viscosity modifier and pour point depressant additives over a temperature range of -40 to 120 °C at shear rate 10 s⁻¹ in a rotational controlled strain rheometer. The group reported that an Arrhenius type equation represents fairly well the variation of oil viscosity at temperatures usually above -5 °C. Vasishth *et al.* [22] studied the viscosity-temperature behaviour of MG 20W-50, SAE 20W-50, MC 20W-50, EP 90 and DXT III industrial lubricants at 20 to 50 °C temperatures and 10 to 100 s⁻¹ shear rates in an Anton-Paar rheometer. They found that the exponential variations of dynamic viscosities with temperature for all test lubricants obey the Arrhenius equation.

The objectives of the present study were to evaluate the rheological properties of synthesized KOTMPE bio-lubricant basestock and to establish a relationship between apparent viscosity and temperature at different shear rates. In addition, the power law was applied to characterize the flow behaviour index of the synthesized bio-lubricant oil sample at different temperatures.

EXPERIMENTAL

The feedstock karanja oil was procured from Kanakdhara Agro Industries, Jaipur (India). The average fatty acid composition of karanja oil (average molar mass 886.71 g/mol) was oleic acid 49.4 %, linoleic acid 19.0 %, palmitic acid 10.6 %, stearic acid 6.8 %, behenic acid 5.3 %, arachidic acid 4.1 %, lignoceric acid 2.4 % and rest 2.4 %. Trimethylolpropane (TMP) (molar mass 134.17 g/mol) was imported from Sigma-Aldrich (Germany). Methanol and anhydrous sodium sulphate were obtained from Merck Specialities Pvt. Limited, Mumbai. The catalyst sulphuric acid abt. 98 % LR was purchased from S.D. Fine-Chem Limited, Mumbai. Silicon high vacuum grease, fuller's earth, potassium hydroxide pellets and phenolphthalein indicator solution were supplied by local chemical supplier. All reagents were used without any purification.

In the reaction scheme, first, the intermediate karanja oil methyl ester (KOME) biodiesel was synthesized from the feedstock karanja oil and then final product karanja oil trimethylolpropane ester (KOTMPE) bio-lubricant basestock was formed. The experimental set-up for the first part of the reaction scheme consisted of a batch type three-necked, 2 L round bottom glass flask. The centre neck was equipped with a reflux condenser to reflux the alcohol vapours back to the flask to prevent any reactant loss. The water to reflux condenser was supplied from an external low temperature water bath. The reflux condenser was also useful in maintaining the atmospheric pressure inside the flask [23]. One side neck was equipped with a thermal sensor to keep a continuous watch over reaction temperature. The other side neck was used as a sampling port.

REMI 2RML heater cum magnetic stirrer was used for heating cum mixing of reactant mass. PTFE coated magnetic stirrer bar was rotated at 600 rpm to overcome the mass transfer limitation of slow reaction rate [14]. A custom-made temperature controller, able to control the temperature within ± 0.1 °C of the set value, was used to maintain the reaction temperature. The set-up for the next part of the reaction scheme required connection of the condenser to a vacuum line equipped with relief valve, accumulator and a vacuum trap.

Synthesis of karanja oil methyl ester: A two-step esterification/transesterification process (acid-catalyzed esterification followed by alkali-catalyzed transesterification) was used on account of free fatty acid content in karanja oil exceeding the barrier of 0.5-1 % [24].

Acid-catalyzed esterification: 0.5 mol of karanja oil, 3 mol of methanol and 1 % H₂SO₄ (w/w karanja oil) were taken as reaction ingredients. The reaction was carried out at 65 °C for a period of 5 h with continuous stirring at 600 rpm. After the completion of the reaction, the reaction mixture was transferred to a separating funnel and allowed to settle overnight under influence of gravity. The water rich top layer was discarded and the lower ester layer was washed with equal volumes of warm water until the discarded rinse water reached a pH level of 6-7. The ester obtained was then dried over anhydrous sodium sulphate and analyzed for its acid and saponification values.

Base-catalyzed transesterification: The prerequisite for base-catalyzed transesterification is an acid value of feed material equal to or less than 2 mg KOH/g oil. The reaction conditions were similar to previous step except for replacement of acid catalyst with base catalyst. 0.5 mol of pretreated oil was transferred into three-necked flask and heated to reaction temperature. 1.25 % KOH (w/w pretreated oil) was dissolved in 3 mol of methanol in a separate beaker and the resulting solution was added to the content of the flask at reaction temperature. The time of reaction was counted from the moment when all the reaction ingredients were added to the flask and the reaction temperature was achieved. After the scheduled period, the reaction mixture was allowed to settle for 8-10 h in a separating funnel by gravity. Two distinct layers were formed due to differences in their density and polarity. The upper layer consisted of KOME, methanol and some soap. The bottom layer consisting glycerol, excess methanol, catalyst, impurities and remains of unreacted oil was separated. The methyl ester layer was then washed with warm water three to four times to remove soaps, salts, free fatty acids, catalyst, glycerol or methanol residuals and dried over anhydrous sodium sulphate. The washing was repeated until the discarded rinse water reached a pH level of 6-7 and no soap bubbles appeared. A clear amber yellow methyl ester was formed.

Synthesis of karanja oil trimethylolpropane ester: Transesterification of KOME with TMP was carried out to obtain KOTMPE bio-lubricant basestock. The following reaction conditions were applied: molar ratio of KOME to TMP 4:1, H₂SO₄ catalyst 2 % (w/w) based on weight of methyl ester, temperature 150 °C, reaction time 3 h and rate of stirring 600 rpm. 0.5 mol of KOME were heated in a three-necked flask to 65 °C. At this temperature 0.125 mol of crystalline TMP were

poured in to the flask. The contents of the flask were continuously stirred to provide uniform mixing and encourage melting of TMP. Now the temperature was set at 150 °C. At 120 °C H₂SO₄ was added to the reaction mixture and reaction was timed from this point onwards. A vacuum of 10 mbar was applied to avoid spillover reaction [25]. The pressure was maintained till the end of the reaction. The methanol produced in the system was continuously withdrawn to enhance the forward reaction and increase methyl ester conversion due to reversible nature of the reaction. The reaction mixture was cooled to ambient temperature upon completion and vacuum filtered to remove the solid materials formed during the reaction. The resulting TMP ester was washed repeatedly with warm water until it was acid free and then dried over a hot plate.

Measurement of viscosity and shear stress with temperature at varying shear rates: The viscosity analyses for bio-lubricant sample were done as a function of temperature range from 10 to 60 °C at constant shear rate of 10, 100 and 1000 s⁻¹. Eleven data points with an interval of 5 °C were selected for analytical purpose. The determination of shear stress corresponding to a shear rate is not difficult [15] and is obtained by multiplying the viscosity with shear rate according to the following relation [26]:

$$\tau = \mu \gamma \quad (1)$$

The measured values of viscosity and shear stress with temperature at three different shear rates are reported in Table-1.

The effect of temperature on apparent viscosity of the synthesized bio-lubricant sample was articulated by the Arrhenius equation applied in following form:

$$\mu = A \exp(E_a/RT) \quad (2)$$

A plot of $\ln$ (apparent viscosity) *versus* $1/(\text{absolute temperature})$ was constructed for test sample at each shear rate. As the cold flow behaviour of bio-lubricant sample was quite different from that at higher temperatures, separate plots were drawn for temperature ranges 10-20 °C and 20-60 °C. A best fit trend line was drawn by connecting the actual data points. Then the slope, intercept and regression coefficient were calculated using this trend line. The magnitude of E_a was calculated by multiplying the slope of the straight line to the gas constant R and A was an exponential of the intercept [20]. The activation energy represents a sort of energy barrier that should be over-powered for an elementary flow process to proceed [15]. The frequency factor is a temperature independent quantity. The

viscosity values of the bio-lubricant sample were predicted using the Arrhenius equation (eqn. 2) at 10, 20, 30, 40, 50 and 60 °C and shear rate variation of 10, 100 and 1000 s⁻¹.

Measurement of viscosity and shear stress with shear rate at varying temperatures - The viscosity measurements were carried out at three different temperatures (27, 60 and 90 °C) in a shear rate range of 100 to 1000 s⁻¹. Nineteen measure points each at an equal interval of 50 rotations per second (rps) were taken with regard to shear rate variation. The shear stress measurements were made following the method described earlier. The values of viscosity and shear stress with shear rate at three different temperatures are reported in Table-2.

Ostwald-deWaele power law model given in eqn. 3 was used to analyze the flow behaviour index of the synthesized bio-lubricating oil basestock at 27, 60 and 90 °C.

$$\tau = K\gamma^n \quad (3)$$

The logarithms were taken on both sides of eqn. 3 and $\log \tau$ *versus* $\log \gamma$ plots were constructed for each temperature value. The intercept of the resulting straight line provided the magnitude of $\log K$ and the slope of the line gave n [19]. Both the consistency index and flow behaviour index are significant fluid properties and are considered constant at a given temperature. The power law classifies the fluids into three different categories based on their flow behaviour index: newtonian ($n = 1$), pseudoplastic ($n < 1$) and dilatant ($n > 1$) [27]. The shear stress values of the synthesized bio-lubricant sample were predicted using power law model (eqn. 3) at shear rate variation of 100, 250, 500, 750 and 1000 s⁻¹ and temperatures of 27, 60 and 90 °C.

RESULTS AND DISCUSSION

Figs. 1 and 2 represent Arrhenius plots for apparent viscosity of the synthesized bio-lubricant sample in temperature ranges of 10-20 °C and 20-60 °C, respectively. The Arrhenius equation was applied to calculate the magnitude of activation energy and frequency factor of the test sample from the trend lines of these plots. The Arrhenius equation parameters obtained from two plots are collected in Table-3. The predicted viscosity values agreed well with the measured viscosity values as evident from Table-4. The high magnitude of R^2 value indicated that changes in apparent viscosity of synthesized bio-lubricating oil with temperature could be modeled suitably using the Arrhenius equation. The study further confirmed the

TABLE-1
VISCOSITY AND SHEAR STRESS *versus* TEMPERATURE MEASUREMENTS AT DIFFERENT SHEAR RATES

Temp. (°C)	Viscosity (Pa·s)			Shear stress (Pa)		
	Shear rate 10/s	Shear rate 100/s	Shear rate 1000/s	Shear rate 10/s	Shear rate 100/s	Shear rate 1000/s
10	2.821	0.885	0.149	28.208	88.495	149.381
15	0.524	0.124	0.053	5.242	12.372	52.954
20	0.035	0.032	0.032	0.354	3.220	31.618
25	0.027	0.026	0.026	0.268	2.608	26.081
30	0.022	0.022	0.022	0.223	2.186	21.839
35	0.019	0.019	0.019	0.188	1.858	18.602
40	0.016	0.016	0.016	0.162	1.595	16.029
45	0.014	0.014	0.014	0.141	1.389	13.938
50	0.012	0.012	0.012	0.124	1.222	12.248
55	0.012	0.011	0.011	0.115	1.084	10.857
60	0.012	0.011	0.010	0.120	1.050	9.897

TABLE-2
VISCOSITY AND SHEAR STRESS *versus* SHEAR RATE MEASUREMENTS AT DIFFERENT TEMPERATURES

Shear rate (1/s)	Viscosity (Pa.s)			Shear stress (Pa)		
	27 °C	60 °C	90 °C	27 °C	60 °C	90 °C
100	0.0244	0.01050	0.00314	2.44	1.05	0.31
150	0.0242	0.01046	0.00332	3.63	1.57	0.50
200	0.0251	0.01136	0.00380	5.02	2.27	0.76
250	0.0252	0.01148	0.00518	6.30	2.87	1.30
300	0.0248	0.01084	0.00576	7.44	3.25	1.73
350	0.0248	0.01049	0.00561	8.68	3.67	1.96
400	0.0248	0.01068	0.00571	9.92	4.27	2.28
450	0.0250	0.01150	0.00617	11.25	5.18	2.78
500	0.0252	0.01227	0.00668	12.60	6.14	3.34
550	0.0253	0.01286	0.00713	13.92	7.07	3.92
600	0.0254	0.01353	0.00757	15.24	8.12	4.54
650	0.0256	0.01395	0.00796	16.64	9.07	5.17
700	0.0257	0.01445	0.00820	17.99	10.12	5.74
750	0.0259	0.01525	0.00837	19.43	11.44	6.28
800	0.0260	0.01575	0.00876	20.80	12.60	7.01
850	0.0262	0.01635	0.00904	22.27	13.90	7.68
900	0.0263	0.01695	0.00925	23.67	15.26	8.33
950	0.0264	0.01745	0.00961	25.08	16.58	9.13
1000	0.0266	0.01785	0.00990	26.60	17.85	9.90

TABLE-3
ARRHENIUS PARAMETERS FOR SYNTHESIZED BIO-LUBRICANT OIL

γ (1/s)	T = 10-20 °C			T = 20-60 °C		
	A (Pa.s)	E_a (J/mol)	R^2	A (Pa.s)	E_a (J/mol)	R^2
10/s	4.05×10^{-56}	303,242.06	0.9651	2.82×10^{-6}	22,706.42	0.9453
100/s	3.71×10^{-43}	229,577.95	0.9768	2.17×10^{-6}	23,274.68	0.9857
1000/s	1.99×10^{-21}	107,581.77	0.9276	1.86×10^{-6}	23,653.21	0.9949

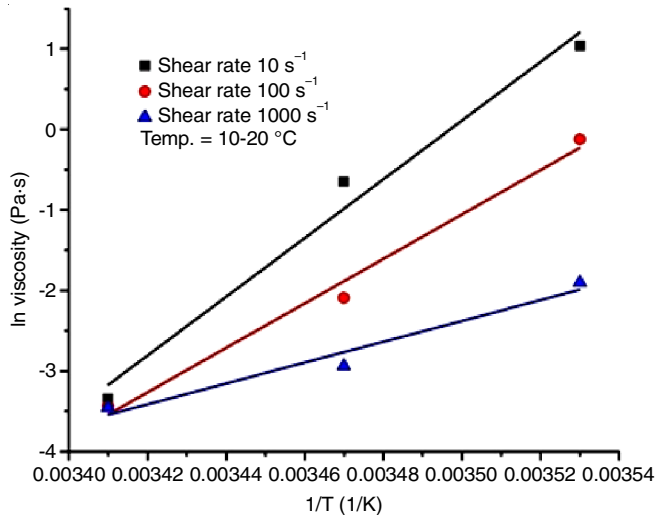


Fig. 1. Arrhenius plot for apparent viscosity of bio-lubricant oil in temperature range of 10-20 °C

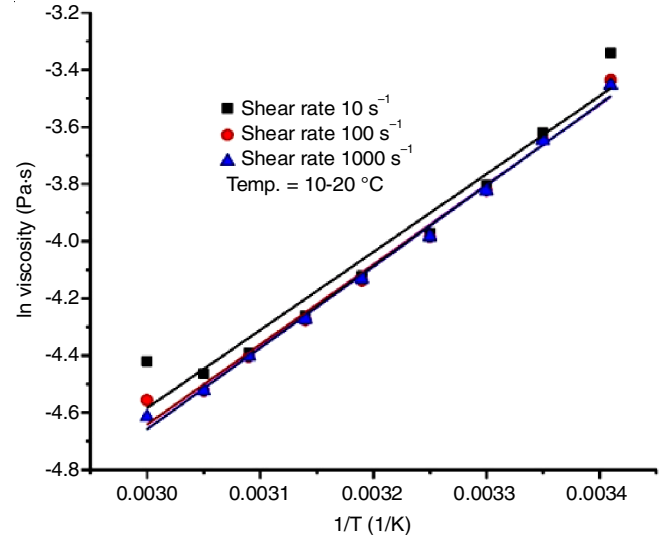


Fig. 2. Arrhenius plot for apparent viscosity of bio-lubricant oil in temperature range of 20-60 °C

TABLE-4
MEASURED AND PREDICTED (IN PARENTHESES)
VISCOSITY DATA (Pa.s) AT DIFFERENT SHEAR RATES

Temp. (°C)	Shear rate 10/s	Shear rate 100/s	Shear rate 1000/s
10	2.821 (3.804)	0.885 (0.881)	0.149 (0.143)
20	0.035 (0.047)	0.032 (0.032)	0.032 (0.030)
20	0.035 (0.032)	0.032 (0.031)	0.032 (0.031)
30	0.022 (0.023)	0.022 (0.022)	0.022 (0.022)
40	0.016 (0.017)	0.016 (0.017)	0.016 (0.016)
50	0.012 (0.013)	0.012 (0.013)	0.012 (0.012)
60	0.012 (0.010)	0.011 (0.010)	0.010 (0.010)

observation that the viscosity of the synthesized bio-lubricating oil was largely influenced by temperature. However, this effect was more pronounced at low temperature and was moderate at high temperatures.

Fig. 3 characterizes the power law behaviour of synthesized bio-lubricant sample at 27, 60 and 90 °C. The power law parameters for the sample are given in Table-5. The flow behaviour index (n) of the bio-lubricant sample ranged from 1.036 to 1.527, which indicated Newtonian fluid behaviour at room temperature that gradually transformed to non-Newtonian

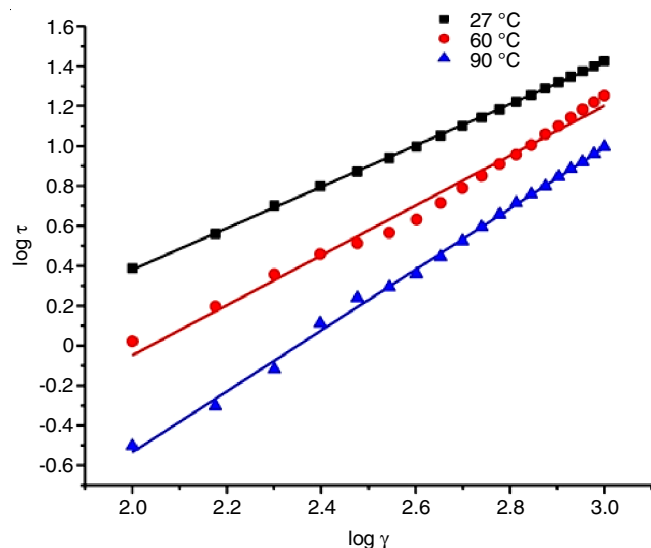


Fig. 3. Power law plot for bio-lubricant oil at 27, 60 and 90 °C

TABLE-5
POWER LAW PARAMETERS

Temp. (°C)	n	K	R ²
27	1.036	20.32×10^{-3}	0.999
60	1.250	2.83×10^{-3}	0.986
90	1.527	0.26×10^{-3}	0.997

behaviour with increase in temperature. The consistency index (K) for the sample was higher at lower temperatures. Little less than elevenfold increase in the magnitude of the K values between 90 and 60 °C was observed, whereas more than sevenfold increase between 60 and 27 °C was observed. Table-6 displays a good harmony between the experimental and the predicted shear stress values.

TABLE-6
EXPERIMENTAL AND PREDICTED (IN PARENTHESIS) SHEAR STRESS VALUES (Pa) AT DIFFERENT TEMPERATURES

Shear rate (1/s)	T = 27 °C	T = 60 °C	T = 90 °C
100	2.44 (2.40)	1.05 (0.89)	0.31 (0.29)
250	6.30 (6.20)	2.87 (2.81)	1.30 (1.19)
500	12.60 (12.71)	6.14 (6.69)	3.34 (3.44)
750	19.43 (19.34)	11.44 (11.11)	6.28 (6.39)
1000	26.60 (26.06)	17.85 (15.91)	9.90 (9.91)

Conclusion

This study characterized the flow behaviour of synthesized karanja oil trimethylolpropane ester (KOTMPE) bio-lubricant basestock. The test sample was analyzed for its viscosity in temperature range of 10–60 °C at shear rates of 10, 100 and 1000 s⁻¹. These data were then fitted in Arrhenius equation and Ostwald-deWaele power law model for flow characterization. The Arrhenius equation provided information on activation energy of the test sample. Karanja oil trimethylolpropane ester bio-lubricant was characterized having high activation energies at low temperatures and low shear rates. The viscosity values predicted with Arrhenius equation agreed substantially with experimental values to establish fitness of Arrhenius parameters. The power law model characterized the KOTMPE bio-lubricant as near Newtonian at room temperature and non-

Newtonian dilatant fluid at high temperatures. The study validated the application of Arrhenius model to predict the apparent viscosity of synthesized KOTMPE bio-lubricant basestock at different temperatures and shear rates as well.

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