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Lubricant properties of Moringa oil using thermal and tribological techniques

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Abstract The increasing application of biobased lubricants could significantly reduce environmental pollution and contribute to the replacement of petroleum base oils. Vegetable oils are recognized as rapidly biodegradable and are thus promising candidates for use as base fluids in formulation of environment friendly lubricants. Although many vegetable oils have excellent lubricity, they often have poor oxidation and low temperature stability. Here in, we report the lubricant potential of Moringa oil, which has 74% oleic acid content and thus possess improved oxidation stability over many other natural oils. For comparison, Jatropha oil, cottonseed oil, canola oil and sunflower oil were also studied. Among these oils, Moringa oil exhibits the highest thermo-oxidative stability measured using PDSC and TG. Canola oil demonstrated superior low temperature stability as measured using cryogenic DSC, pour point and cloud point measurements. The friction and wear properties were measured using HFRR. Overall, it was concluded that Moringa oil has potential in formulation of industrial fluids for high temperature applications.

Keywords Oxidation stability · Cloud point · Pour point · DSC · HFRR

Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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Introduction

Deliberate and accidental lubricant losses occurring due to evaporation, leakages and spills are causing pollution and environmental health concerns. Every year about 5–10 million tons of petroleum products enter into the environment from spills, industrial and municipal waste, urban runoff, refinery processes, and condensation from marine engine exhaust [1, 2]. In certain applications, strict specifications on various environmental matters, such as biodegradability, toxicity, occupational health and safety, and emissions, have become mandatory. This has stimulated the search for environmentally friendly lubricants. Other factors adding to search for alternative energy sources are uncertainty in petroleum supply, high prices of petroleum crude oils (>$140/barrel), and political considerations. Vegetable oils are a renewable resource and thus finding a way into lubricants for industrial and transportation needs [3]. Vegetable oil-based products are environment friendly and non-toxic and thus offer easier disposal as compared to petroleum products. There are also biodegradable synthetic

oils offering improved stability and performance characteristics over refined petroleum oils but prices for these niche products are higher than vegetable oils and significantly higher than petroleum-based lubricants [4].

At present over 125 million metric tons of vegetable oils are produced worldwide. These vegetable oils offer excellent lubricity, biodegradability, favorable viscosity temperature characteristics, high flash points, and compatibility with mineral oil and additive molecules. The restriction in using vegetable oils for formulating lubricants are their insufficient thermal and oxidative stability [5], low temperature fluidity, and hydrolytic instability [6]. Some of these restrictions can be overcome by using high oleic varieties of vegetable oils in combination with available additives (antioxidants, pour point depressants) and diluents or functional fluids [7].

Moringa oleifera (referred to as Moringa in this study), a member of the Moringaceae family is a multipurpose plant native to sub-Himalayan regions of Northwest India, Africa, Arabia, Southeast Asia, the Pacific and Caribbean islands, and South America. It also has been distributed in many other regions such as the Philippines, Cambodia, and Central and North America [8]. In Pakistan, it is mainly grown in plain areas of Punjab, Sindh and Baluchistan, and to some extent in Northwestern Frontier Province [9]. It is esteemed nutritionally as an important food commodity, and also has many medicinal uses [10]. The fully matured, dried seeds of this plant are round or triangular shaped, and the kernel is surrounded by a lightly wooded shell with three thin flexible wings [11, 12]. Moringa seeds contain between 33 and 41% (w/w) of vegetable oil [12]. Several authors investigated its composition including fatty acid profile [9, 12–14] and found its oil to be high in oleic acid (>70%). Its oil is commercially known as "ben oil" or "behen oil," due to its content of behenic (docosanoic) acid. It possesses significant resistance to oxidative degradation [15], and has been extensively used in the enfleurage process [11]. A recent survey conducted on 75 indigenous (India) plant-derived nontraditional oils concluded that *M. oleifera* oil, among others, has good potential for biodiesel production [16].

The potential of Moringa oil as feedstock for preparing biodiesel has been discussed previously [17]. Moringa oil derived biodiesel has a high cetane number and enhanced oxidative stability compared to other biodiesels. In this study we report the evaluation of Moringa oil compared to other vegetable oils for its possible application as base oil in lubricant formulations. The fatty acid compositions, free fatty acids, iodine values, peroxide values, kinematic viscosity were determined for the oils in question. Oxidative stability of vegetable oils were evaluated using pressure differential scanning calorimetry (PDSC), thermo gravimetric analysis (TG), and oxidation stability index. The low temperature flow properties were studied using cryogenic DSC, pour point, and cloud point measurements, while friction and wear properties were measured using the HFRR.

Experimental

Materials

Moringa oleifera and *Jatropha curcas* seeds were obtained from the University of Agriculture (Faisalabad, Pakistan) and samples of cotton-, canola- and sunflower seeds were procured from Ayub Agricultural Research Institute (AARI), Faisalabad, Pakistan. Pure standards of FAME were purchased from Sigma Chemical Company (St. Louis, MO). All other chemicals and reagents (*n*-hexane and anhydrous sodium sulfate) were analytical reagent grade and purchased from Merck Chemical Company (Darmstadt, Germany). All chemicals and regents were used as received.

Extraction of vegetable oils

All seeds samples (500 g) were crushed and placed in a Soxhlet extractor fitted with a 2-L round-bottomed flask and a reflux condenser. After extraction in a water bath for 6 h with 0.80 L of *n*-hexane, the solvent was removed at 45 °C under vacuum using a rotary evaporator (Eyela, N–N Series, Rikakikai Co. Ltd., Tokyo, Japan). The oils were used as received after extraction without any further purification.

Physico-chemical characterization of oils

The kinematic viscosity of vegetable oils was measured using Cannon-Fenske calibrated viscometers (Cannon Instrument Co., State College, PA) in a Cannon temperature bath (CT-1000) at 40 and 100 °C according to ASTM standard method D445-95. The viscosities obtained are average values of 2–3 determinations and the precision is within the limits of ASTM method specification. To compare base oils with respect to viscosity variations with temperature, ASTM method D2270 provides a means to calculate a viscosity index (*VI*). *VI* was thus calculated using kinematic viscosity at 40 and 100 °C.

Pour and cloud points were measured by following the ASTM D-5949 method using Phase Technology Analyzer, Model 70X (Phase technology, Hammersmith Gate, Richmond, B.C., Canada). The pour point is defined as the temperature in °C when the sample still pours when the jar is tilted. Statistically the method has shown quite good consistency for determining low temperature flow property of fluids.

The free fatty acid content, iodine value and peroxide value for the vegetable oils were determined as per AOCS official methods Ca 5a-40, Cd 1-25 and Cd 3-25, respectively.

Fatty acid methyl esters (FAMEs) were prepared according to the standard of IUPAC method 2.301 and analyzed on a SHIMADZU gas chromatograph model 17-A, equipped with flame ionization detector (FID). Separation was done on a methyl-lignocerate-coated polar capillary column SP-2330 (30 m × 0.32 mm × 0.20 μm; Supelco, Inc., Bellefonte, PA., USA.). Nitrogen was used as a carrier gas at a flow rate of 3.0 mL min^{-1}. Column temperature was programmed from 180 to 220 °C at the rate of 5 °C min^{-1}. Initial and final temperatures were held for 2 and 10 min, respectively. Injector and detector were set at 230 and 250 °C, respectively. A sample volume of 1.0 μL was injected using split mode (split ratio of 1:75). FAMEs were identified by comparing their relative and absolute retention times to those of authentic standards. Heptadecanoic acid (C17:0) was used as an internal standard. The external calibration method was adopted for standardization. The quantification was done by a Chromatography Station for Windows (CSW32) data handling software (Data Apex Ltd. CZ-158 00 Prague 5, Czech Republic). The fatty acid composition is reported as a relative percentage of the total peak area.

Thermal stability was measured using TG. Dry nitrogen (Gateway Airgas, St. Louis, MO) was used for balance chamber at a flow of 40 mL min^{-1}, while dry air was used over sample at flow of 60 mL min^{-1}. A 10 μL of sample was used in platinum pans. The temperature was equilibrated at 50 °C, and then increased to 600 °C at a ramp rate of 10 °C min^{-1}. The onset (T_{onset}) and end (T_{end}) temperatures were reported.

The oxidative stability was measured using PDSC (DSC 2910 thermal analyzer, TA Instruments, New Castle, DE). A 2 μL sample in pinhole hermetically sealed aluminum pan was oxidized in the presence of air (1378.95 kPa, 200 psi) by heating at ramp rate of 10 °C min^{-1}. The onset temperature (*OT*) of oxidation was obtained from extrapolating the tangent drawn on the steepest slope of reaction exotherm. High *OT* would suggest a high oxidative stability of the vegetable oil.

The oxidative stability of the vegetable oils samples were also determined with the Model 743 Rancimat (Metrohm AG, Herisau, Switzerland) following standard EN14112. The samples of 3 g, held in heating block at 110 °C, were analyzed under constant airflow of 10 L h^{-1}. All determinations of induction period were performed in triplicate and the mean oxidative stability index (*OSI*) values reported.

Before each cryogenic DSC experiment, the DSC cell was purged with low-pressure nitrogen gas. A 10 mg oil sample was accurately weighed in an open aluminum pan and placed in the DSC module with a similar empty pan as reference. The procedure involved rapidly heating the sample to 50 °C and then holding the sample under isothermal condition for 10 min. This helps in dissolving and homogenizing any waxy material present in the oil, which may inadvertently act as seed to accelerate wax crystal formation during cooling. The system was then cooled to − 80 °C at a steady rate of 10 °C min^{-1} using liquid nitrogen as the cooling medium. The heat flow (W g^{-1}) versus temperature for each heating cycle was analyzed to determine wax disappearance temperature (*WDT*, °C) and signal maxima temperature (*SMT*, °C). The average value of three independent measurements was taken in each case.

Lubricity determination were performed at 60 °C, according to ASTM method D 6079 using a high-frequency reciprocating rig (HFRR) lubricity tester (PCS Instruments, London, UK) via Laser Scientific (Granger, IN, USA). The average wear scar (μm) diameter of each replicates was determined by calculating the average of the x- and y-axis wear scar lengths. Each experiment was conducted in triplicate and the data is reported as mean ± SD of triplicate determinations.

Results and discussion

Oxidation stability and poor low temperature properties are some of the drawbacks of using vegetable oils in lubricants. The poor oxidation stability is mainly due to bis-allylic carbons present between two double bonds, while one of the causes of poor flow properties are presence of saturated fatty acids. Therefore, if oxidation stability is improved by saturating the double bonds using hydrogenation, the low temperature properties get worse. It has been shown in previous studies that presence of more oleic acid is ideal in terms of improved oxidative stability [9]. As Moringa oil has high oleic acid content, it merits detailed evaluation as potential lubricant base oil.

Fatty acid composition

Table 1 shows the fatty acids of composition of Moringa oil along with Jatropha, cottonseed, canola and sunflower oil. The major fatty acid (FA) in Moringa oil is oleic (74%) with negligible amounts of linoleic and linolenic. The detected fatty acids are grouped into three major categories: saturated FA (*SFA*) containing myristic ($C_{14:0}$), palmitic ($C_{16:0}$), stearic ($C_{18:0}$), arachidic ($C_{20:0}$), and behenic ($C_{22:0}$) acids; monounsaturated FA (*MUFA*) containing palmitoleic ($C_{16:1}$), oleic ($C_{18:1}$), and gadoleic ($C_{20:1}$); and polyunsaturated FA (*PUFA*) containing linoleic ($C_{18:2}$) and linolenic ($C_{18:3}$) acids. The distribution of these categories

Table 1 Fatty acid (FA) composition of vegetable oils by GC analysis

FA	Moringa oil	Jatropha oil	Cottonseed oil	Canola seed oil	Sunflower seed oil
$C_{14:0}$	ND	ND	0.74 ± 0.01	ND	ND
$C_{16:0}$	6.65 ± 0.12	12.15 ± 0.23	25.64 ± 0.30	4.32 ± 0.08	7.09 ± 0.13
$C_{16:1}$	ND	ND	0.68 ± 0.01	ND	ND
$C_{18:0}$	6.09 ± 0.08	16.8 ± 0.24	2.88 ± 0.06	1.96 ± 0.02	4.32 ± 0.14
$C_{18:1}$	73.85 ± 0.96	13.00 ± 0.17	17.77 ± 0.35	55.57 ± 0.70	34.98 ± 0.52
$C_{18:2}$	0.99 ± 0.02	49.75 ± 1.04	50.44 ± 0.80	19.98 ± 0.41	51.96 ± 1.09
$C_{18:3}$	ND	ND	0.38 ± 0.01	9.43 ± 0.18	1.11 ± 0.02
$C_{20:0}$	3.98 ± 0.02	5.01 ± 0.10	0.46 ± 0.01	1.61 ± 0.02	0.51 ± 0.01
$C_{20:1}$	1.99 ± 0.01	2.00 ± 0.03	ND	ND	ND
$C_{22:0}$	5.85 ± 0.01	0.58 ± 0.01	ND	2.21 ± 0.04	ND
SFA[a]	22.6	34.5	29.7	10.1	11.9
MUFA[b]	75.8	15.0	18.5	55.6	35.0
PUFA[c]	1.0	49.8	50.8	29.4	53.1
UFA[d]	76.8	64.8	69.3	85.0	88.1
UN[e]	78	115	120	124	142

ND not detected; values are mean ± SD of triplicate determinations, expressed as % w/w with coefficient of variation <5% except *UN*

[a] *SFA*, saturated FA ($C_{14:0} + C_{16:0} + C_{18:0} + C_{20:0} + C_{22:0}$)

[b] *MUFA* monounsaturated FA ($C_{16:1} + C_{18:1} + C_{20:1}$)

[c] *PUFA* polyunsaturated FA ($C_{18:2} + C_{18:3}$)

[d] *UFA* monounsaturated FA (*MUFA* + *PUFA*)

[e] *UN* unsaturation numbers ($1 \times (MUFA) + 2 \times (C_{18:2}) + 3 \times (C_{18:3})$)

SFA, *MUFA* and *PUFA* in these oils is shown in Fig. 1. Jatropha oil (35%) has highest amount of saturated fatty acids (*SFA*) followed by cottonseed (30%), Moringa (23%), sunflower oil (12%) and least amount in canola oil (~10%). Although Moringa oil has 77% unsaturated FA (*UFA*), most of it is monounsaturated (*MUFA*) with little (1%) polyunsaturated FA (*PUFA*). *MUFA* are highest in Moringa oil (76%) followed by canola (56%), sunflower (35%), cottonseed (18%), and least in Jatropha oils (15%). *PUFA* are high in Jatropha, cottonseed, and sunflower oil (50–53%) followed by canola oil (29%) and least in Moringa oil (1%). The unsaturation numbers (*UN*) of these oils were also calculated using fatty acid composition shown in Table 1. The *UN* is highest for sunflower oil (142) followed by canola (124), cottonseed (120), and Jatropha (115), and least for Moringa oil (78). The effect of fatty acid composition on various properties will be discussed.

Viscosity and other properties

Table 2 shows some typical properties of these oils. Except Jatropha oil, all other oils have low free fatty acids. The peroxide value is also higher for Jatropha compared to other oils. The iodine value is high for sunflower oil, followed by cottonseed, Jatropha, and canola and least for Moringa oil. The kinematic viscosity at 100 °C for all the samples is around 8 cSt, while at 40 °C is around 35 cSt except Moringa oil, which had 27 cSt, thus providing it higher viscosity index (*VI*) compared to other oils. The high viscosity index of Moringa oil will enable it to be formulated in multigrade lubricants applications.

These properties were correlated to the fatty acid composition in terms of *SFA*, *UFA*, *MUFA*, *PUFA*, and *UN*. As expected, the best correlation was found between *UN* and iodine value ($R^2 = 0.90$). The kinematic viscosity at 40 °C also correlates linearly with *UN* with R^2 value of 0.95. Similar correlation was found between *PUFA*-IV (R^2 value of 0.88) and *PUFA*-KV40 ($R^2 = 0.81$). Viscosity index also correlated well with *PUFA* (R^2 value of 0.88) and *MUFA* (R^2 value of 0.78). Increase in *MUFA* and decrease in *PUFA* increases the viscosity index of the oils. These results show that some of the properties can be correlated well to the fatty acid composition, which in turn can be utilized to develop models to predict these physical properties.

Thermal and oxidative stability

Figure 2 shows PDSC curves for Moringa and other vegetable oils, and Table 3 shows the PDSC-onset temperature data. The onset temperature which is a measure of oxidative stability is at least 20 °C higher for Moringa oil than other oils. Similar results were obtained from the oxidative stability index (*OSI*) measured using Rancimat method EN

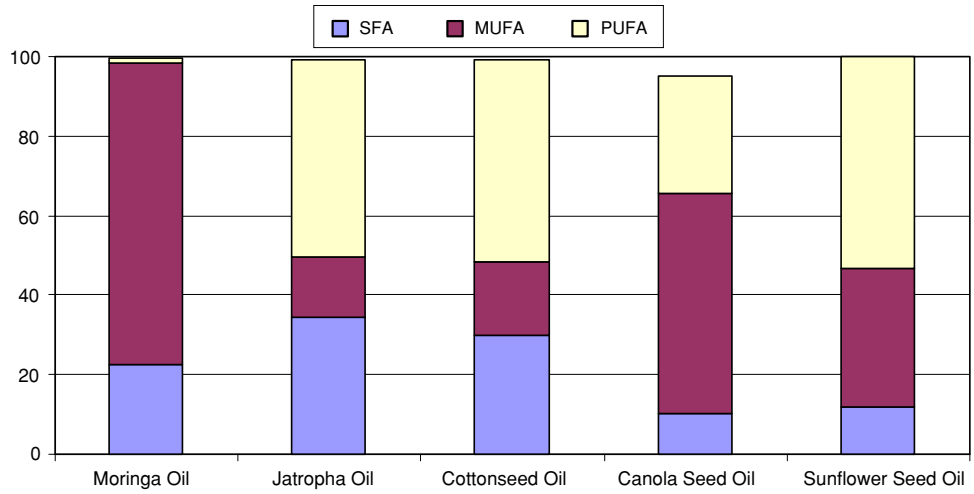

Fig. 1 Distribution of saturated FA (*SFA*), monounsaturated FA (*MUFA*), and polyunsaturated FA (*PUFA*) in Moringa and other vegetable oils

Table 2 Viscosity and other physicochemical properties of oils

Oil sample name	*FFA* (%)	PV	IV	KV40 (cSt)	KV100 (cSt)	*VI*
Moringa	0.32 ± 0.3	1.65 ± 0.05	70 ± 1	27.1 ± 1.2	7.0 ± 0.1	239
Jatropha	3.95 ± 0.15	4.26 ± 0.12	107 ± 3	34.6 ± 1.3	8.0 ± 0.2	213
Cottonseed	0.61 ± 0.05	1.12 ± 0.15	111 ± 3	34.3 ± 1.3	8.0 ± 0.5	216
Canola	0.38 ± 0.10	1.3 ± 0.05	99 ± 2	34.9 ± 1.2	8.1 ± 0.6	219
Sunflower	0.45 ± 0.07	2.5 ± 0.11	130 ± 3	36.8 ± 1.1	8.5 ± 0.6	218

Values are mean ± SD of triplicate determinations

FFA Free fatty acid (% as oleic acid) with standard deviation (*SD*) < 0.15, *PV* Peroxide value expressed as milliequivalents peroxide per 1,000 g sample (m eq kg^{-1} of oil) with *SD* < 0.15, *IV* Iodine value expressed as % iodine absorbed (g of I_2/100 g of oil) with *SD* < 3, *KV* Kinematic viscosity, *VI* Viscosity index

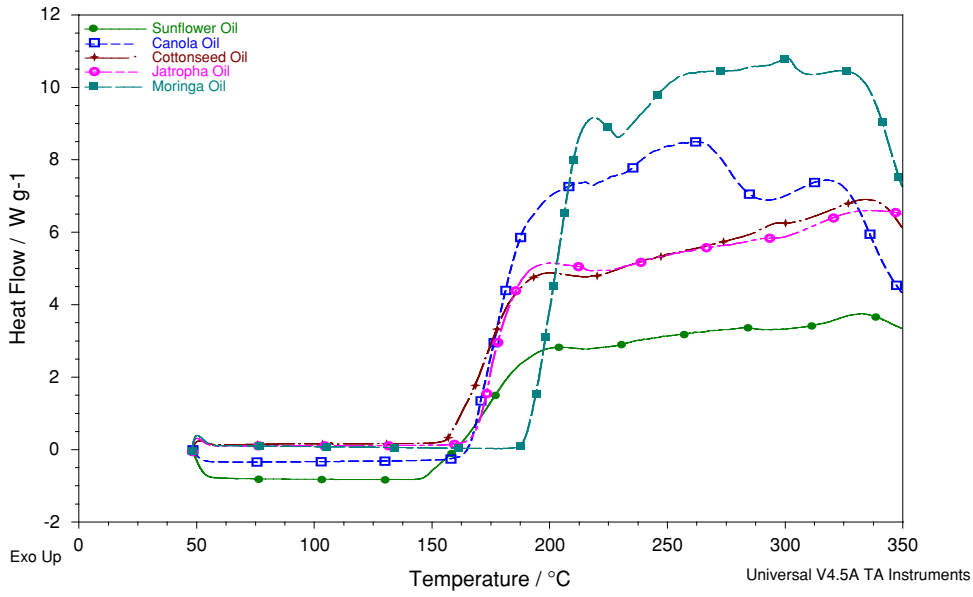

Fig. 2 Typical PDSC curves for Moringa and other vegetable oils

14112. The PDSC technique uses microgram amount of sample, while Rancimat uses 3 g of sample. PDSC as well as Rancimat tests were run in triplicate and the values shown are average of three measurements. The maximum standard deviation (*SD*) obtained in *OT* measurement is 1.2 °C for canola oil, while for other oils it is less than 0.7 °C. The coefficient of variation (*CV*) for PDSC measurements vary from 0.2–0.7%. For OSI measurements,

Table 3 Oxidation and thermal stability of oils measured using PDSC, Rancimat and TG

Oils	*OT* (°C)	*OSI* (h)	T_{onset} (°C)	T_{end} (°C)
Moringa oil	191 ± 0.4	15.3 ± 1.288	347	393
Jatropha oil	169 ± 0.3	2.6 ± 0.055	322	413
Cottonseed oil	159 ± 0.4	1.9 ± 0.044	343	406
Canola oil	164 ± 1.2	3.4 ± 0.01	339	391
Sunflower oil	153 ± 0.7	1.1 ± 0.01	342	403

Values are mean ± SD for triplicate determinations

except Moringa oil (*SD* 1.3 h), all other oils have *SD* less than 0.06 h. Moringa oil thus showed higher *CV* (8.4%) than other oils (0.3–2.3%). This shows that oxidative stability data generated using PDSC is more repeatable than *OSI*. It has been shown in an earlier study that higher stability oils like Moringa oil show poor repeatability in Rancimat test [18], while the PDSC method can be used for low as well as very high oxidative stability oils. The PDSC onset temperature shows good correlation with Rancimat *OSI* values (R^2 value of 0.91). The higher oxidative stability shown by Moringa oil is ascribed to its low unsaturation number (78) compared to other oils and presence of naturally occurring antioxidants [15]. This low unsaturation number is the result of higher amounts of *MUFA* and *SFA* present in it. The unsaturation number correlates very well with the *OT* ($R^2 = 0.95$) and *OSI* data ($R^2 = 0.87$). The highest unsaturation number of sunflower seed oil makes it least oxidative stable with low *OT* and *OSI* values.

The thermal stability of the oils is important in defining the operability conditions for the lubricants prepared using such vegetable oils [19–23]. Hence, the thermal stability of Moringa oil along with other vegetable oils was measured using TG under inert atmosphere of nitrogen. A typical TG curve of Moringa oil is shown in Fig. 3, which provides results shown in Table 3. All oils show a temperature range of particular length before any mass loss occurs. This induction period is followed by a steep fall in the curve with varying slope, which indicate losses due to either evaporation or cracking. The slope and behavior of the curve do not show any indication whether a distillation mass loss is continuing or the sample has already been thermally cracked. T_{onset} marks the onset temperature of the thermal mass loss transition, while T_{end} marks the end temperature of the transition. Apart from thermal stability of oil, T_{onset} also provides an idea of initial boiling point of oil. The thermal stability as measured using T_{onset} do not correspond to oxidative stability data, although Moringa oil with lowest *UN* and highest oxidative stability showed highest T_{onset} value. This is because of the different atmosphere used in these analyses. The mass loss temperatures closely corresponds to distillation curves and can be used to see the boiling range of the oils [24].

Low temperature properties

Table 4 shows the pour and cloud points of the Moringa oil and other vegetable oils. Moringa oil showed higher pour point than other oils despite the fact that it has a high *UFA*. This high pour point is due to presence of ~23% *SFA*. Although two other oils tested have a higher amount of *SFA*, but larger amount of *PUFA* lowers their pour points. For example, Jatropha oil also has 35% *SFA*, but out of 65% *UFA*, there are 15% *MUFA* and 50% *PUFA*, and presence of such higher amount of *PUFA* results in a lower pour and cloud point. It appears that pour and cloud point is influenced by the amount of saturate or mono-unsaturate or poly-unsaturate fatty acids and not by their chain lengths

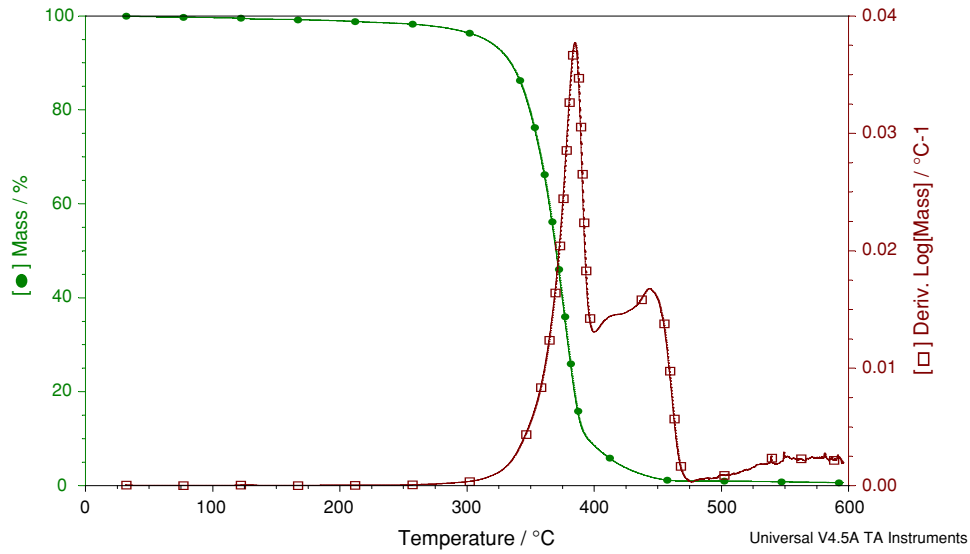

Fig. 3 Typical TG and DTG curves of Moringa oil

Table 4 Low temperature properties of vegetable oils shown using wax disappearance temperature (*WDT*) and signal maxima temperature (*SMT*) measured using Cryo-DSC, and pour point (PP), cloud point (CP) measured using ASTM D5949

Sample name	PP (°C)	CP (°C)	*WDT* (°C)	*SMT* (°C)
Moringa oil	4	5	−11.7 ± 0.3	−0.7 ± 0.2
Jatropha oil	−11	−6.4	−43.1 ± 0.9	−25.7 ± 0.4
Cottonseed oil	1	7.7	−6.6 ± 0.1	−1.7 ± 0.0
Canola seed oil	−13	−13	−28.9 ± 0.1	−19.8 ± 0.1
Sunflower seed oil	−10	−4.5	−24.0 ± 0.1	−16.2 ± 0.1

Values are mean ± SD for triplicate determinations

[25]. Therefore a low amount of *SFA* with a good combination of *MUFA* and *PUFA* favor low pour and cloud points.

The crystallization behavior of Moringa oil and other vegetable oils was also studied using Cryo-DSC [26]. The long chain compounds (FA chains) of vegetable oils in the solid state exist in more than one crystalline form and thus have multiple melting points. The melting points of triacylglycerol depend on chain length, nature of unsaturation (cis or trans olefin), number and position of double bonds [27, 28]. Monoacid triacylglycerols show three distinct melting points corresponding to the three crystalline forms α, β', and β [29, 30]. Since most vegetable oils are mixed triacylglycerols, therefore no β form is present and have highest melting β'form [31]. When the oil is cooled quickly it solidifies in the lowest melting α form. When heated slowly the mono-acid triacylglycerols melts and held just above the α melting point, it resolidifies in the β'crystalline form. The β form is the highest melting form in case of monoacid triacylglycerols and is produced by crystallization from solvent. Since crystallization kinetics is very sensitive to temperature fluctuation, cooling rate or thermal history, Cryo-DSC method is relatively simple, reproducible and robust enough to provide good control on temperature fluctuation, cooling rate etc.

Cryo-DSC has been utilized earlier for identification of various crystallization forms of pure single acid triacylglycerol [30, 32, 33]. Since vegetable oils are mixtures, situation becomes complex. DSC curves (heating cycle) for vegetable oils are shown in Fig. 4a and b. Multiple transitions have been observed during cooling and heating cycle of DSC experiment as shown in Fig. 4a (cottonseed oil). Three measurements (heating and cooling cycle) were done for each oil. It was found that more variation in results was observed in the cooling cycle than the heating cycle. In case of cooling cycle, 8 out of 16 data points (50%) showed standard deviation higher than 1 °C runs and it varied from 1.2 to 14.2 °C. For the heating cycle, only one out of 20 (5%) showed standard deviation of 1.5 °C. A previous study [34] also showed that in a heating experiment, DSC curves are minimally affected by thermal history and variations in cooling rate, while in cooling experiment, these factors can influence the shape of the peak and cause more variation in the results. Therefore for this study also, only the results obtained from heating cycle will be used to analyze the influence of fatty acid composition on cold flow properties of vegetable oils. The wax disappearance temperatures (*WDT*) and signal maxima temperatures (*SMT*) of various peaks are shown in Table 4. Moringa oil shows single sharp peak at *SMT* of −0.7 °C and *WDT* of −11.7 °C (Fig. 4a) because of predominant oleic acids. The broadest peak is shown by Jatropha oil (Fig. 4b) at *SMT* of −25.7 °C and *WDT* of −43.1 °C possibly due to wide variation in fatty acid chain lengths, and it appears to be mix of three peaks corresponding to linoleic (lowest temperature), oleic, and stearic. Jatropha and Moringa oil have almost same amount of *SFA* and *UFA*, but the makeup of *UFA* is different. In Jatropha oil, *MUFA* are 15%, while *PUFA* are 50%, while in Moringa oil, *MUFA* are 76% and *PUFA* are 1%. This change in composition of *UFA*, i.e. lower amount of *PUFA* in Moringa oil results in higher *SMT* and *WDT* values compared to Jatropha oil. Sunflower oil contains both *MUFA* (35%, all oleic) and *PUFA* (53%, mostly linoleic 52%) in considerable amount, and both types have different packing characteristics in crystallization. This results in a broad peak (Fig. 4b), which appears to be a mix of two peaks (corresponding to oleic and linoleic) giving it a shape of blunt two-headed peak at *SMT* of −16.2 °C and *WDT* of −24 °C. Cottonseed oil contain all three classes of fatty acids (*SFA* 30%, *MUFA* 18%, *PUFA* 51%) in high amounts and thus results in three separate peaks (Fig. 4a) corresponding to *SFA* (palmitic acid with higher melting point; *SMT* −1.7 °C; and *WDT* −6.6 °C), *MUFA* (oleic acid; *SMT* −22.3 °C; and *WDT* −26.0 °C) and *PUFA* (linoleic acid; *SMT* −39.1 °C; and *WDT* −50.2 °C). Higher amount of *SFA* in cottonseed oil resulted in higher *SMT* (−1.7 °C) and *WDT* (−6.6 °C). More *SFA* in an oil results in close packing of the triacylglycerol molecules during cooling leading to gel like structures entrapping low melting molecules also and thus results in higher pour points, cloud points, *WDT* and *SMT*. *PUFA* in their bent configuration prevents the close packing of triacylglycerol molecules during cooling more than *MUFA*, thus high *PUFA* in oils (such as Jatropha and sunflower oil) results in lower pour point, cloud point, *SMT*, and *WDT*.

SMT obtained using Cryo-DSC was found to be a better measure of pour point as shown by better correlation ($R^2 = 0.90$) than *WDT* ($R^2 = 0.70$). Similarly cloud point also showed better correlation with *SMT* ($R^2 = 0.78$) than *WDT* ($R^2 = 0.64$). In all these correlations, the major outlier point was of Jatropha oil. On removing this point, the R^2 value for PP-*SMT* correlation increased to 0.99, PP-

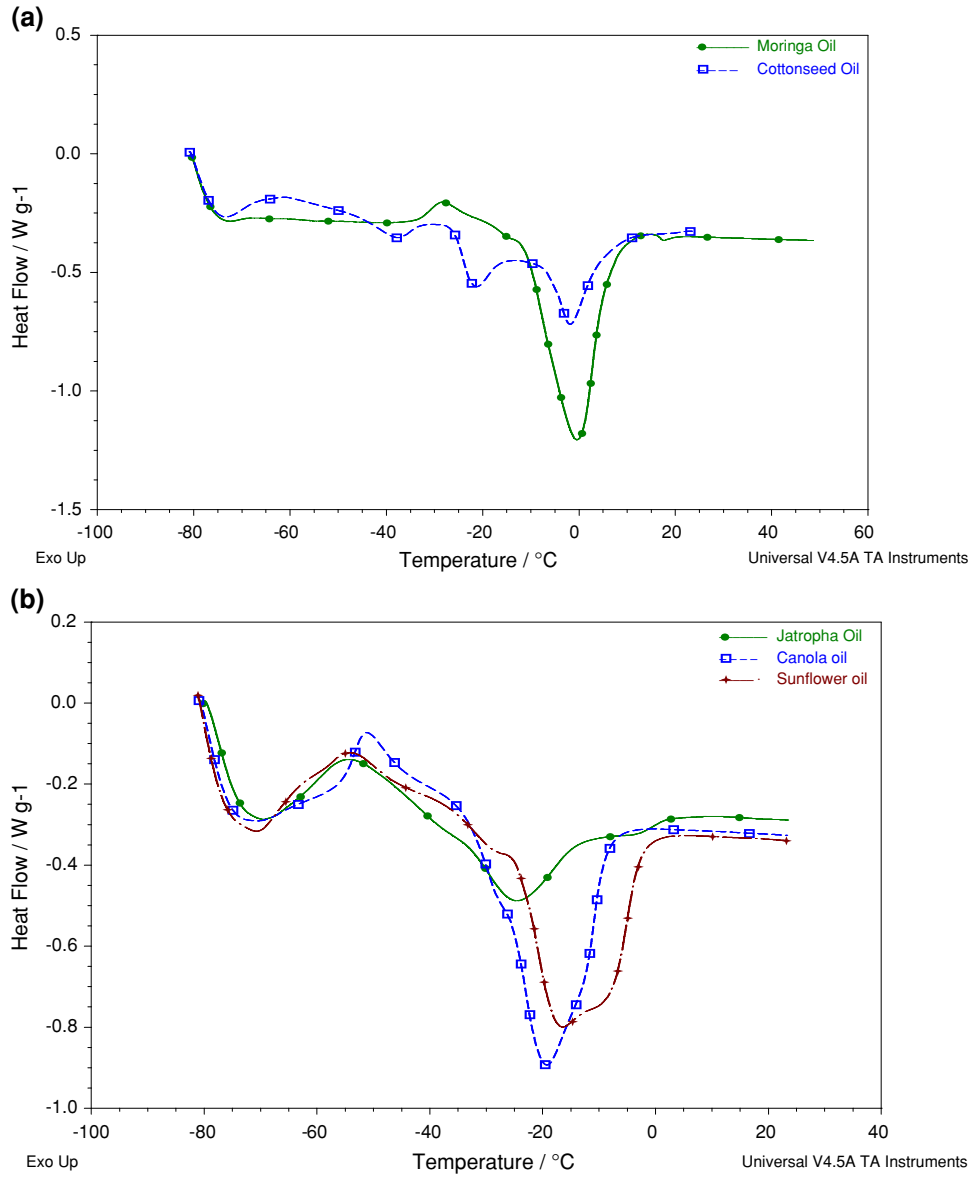

Fig. 4 **a** Cryo-DSC curve of Moringa and cottonseed oil showing various transitions. **b** Cryo-DSC curve of Jatropha, canola and sunflower oil

WDT to 0.88, CP-*SMT* to 0.92, and CP-*WDT* to 0.96. More oil samples will help develop better correlations between two methods.

Lubricity data

An important property of lubricants is their ability to maintain a stable lubricating film at the metal contact zone. Triacylglycerols of vegetable oils are known to provide excellent lubricity due to their ester functionality. This is because, the polar head of the triacylglycerol molecule, i.e. glycerol end attach to metal surfaces and allow a monolayer film formation with the non-polar end of fatty acid chains sticking away from the metal surface. This prevents the metal-to-metal direct contact by providing a sliding surface. Without a good sliding surface, the two metals at the contact zones of moving parts come in direct contact with each other and results in increase in temperature causing adhesion, scuffing or even welding. The ester structures in triacylglycerol offers active oxygen sites that trigger binding on the metal surface forming a protective film. This protective film builds further with time to reduce friction.

The antiwear and friction reducing properties of Moringa oil and other vegetable oils were evaluated using high-frequency reciprocating rig (HFRR) lubricity tester. The HFRR method determines the lubricity or the ability of a fluid to affect friction and wear between the surfaces in relative motion under load. The average ball scar diameter, width of wear track on disk at x-axis, film percentage, and coefficient of friction (*CoF*) for Moringa and other vegetable oils are shown in Table 5. With Moringa oil, the ball

Table 5 HFRR lubricity data on vegetable oils

Sample	Ball wear scar diameter (μm)	Disc wear scar width on X-axis (μm)	Disc wear scar length on X-axis (μm)	Film (%)	*CoF*
Moringa oil	156 ± 2	217 ± 2	1144 ± 49	97	0.092
Jatropha oil	146 ± 3	204 ± 2	1168 ± 34	97	0.096
Cottonseed oil	202 ± 2	253 ± 3	1142 ± 40	95	0.097
Canola oil	149 ± 3	173 ± 2	1202 ± 51	94	0.076
Sunflower oil	151 ± 3	192 ± 2	1134 ± 44	95	0.069

Values are mean ± SD of triplicate determinations

scar diameter was 156 μm, which is similar to other vegetable oils except cottonseed oil, which had ball scar diameter of 202 μm. This high wear scar diameter for cottonseed oil may be due to low amount of free fatty acids (*FFA*) present in it. The Jatropha oil provided the lowest wear scar diameter, which may be due to presence of higher amount of *FFA* present in it. The disk x-scar results were also similar, with biggest scar width for cottonseed oil. The average *CoF* is higher (0.09) for Moringa, Jatropha and cottonseed oil, followed by canola oil (0.076) and least for sunflower oil (0.07). The lower *CoF* in sunflower and canola oil may be due to their higher viscosity compared to other oils. Despite the higher *CoF* for Moringa oil, no decrease was observed in the average lubricant film percentage. An attempt was made to see the effect of various groups of fatty acids, i.e. *SFA*, *UFA*, *MUFA*, and *PUFA* on lubricity properties of these oils. The *CoF* was found to have good correlation with *SFA* ($R^2 = 0.85$) and *UFA* ($R^2 = 0.89$). This correlation shows that low amount of *SFA* and high amount of *UFA* results in low *CoF*. High *UFA* and low *SFA* amounts may be the reason for lower *CoF* in case of canola and sunflower oil. More studies are needed to confirm this observation. These results show that lubricity properties of Moringa oil are at par with other vegetable oils.

Conclusions

In this study we have evaluated the potential of Moringa oil as base oil for lubricant applications. The oxidative, thermal, low temperature and lubricity properties were compared with four other vegetable oils. The Moringa oil has kinematic viscosity in the range suitable for formulating lubricant of ISO viscosity grade 32. The viscosity index of Moringa oil is much higher compared to other vegetable oils studied, making it suitable for use as multi-grade lubricant. The Moringa oil showed excellent thermal and oxidative stability because of the presence of high amount of *MUFA* in it. The oxidative stability measured using PDSC and Rancimat showed good correlation between two methods. The low temperature properties were studied using pour, cloud point determinations as well as Cryo-DSC and a good correlation was found between two methods. The pour and cloud points for Moringa oil are higher and needs further treatment, such as use of pour point depressant, or other diluents to lower the pour point. The lubricity or Moringa oil is similar to other vegetable oils. Thus, Moringa oil has good potential for use as lubricant base oil and an acceptable alternative to food oils and high priced petroleum base oils.

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