

Soybean Oil Based Greases: Influence of Composition on Thermo-oxidative and Tribochemical Behavior

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The biodegradable properties and lubricating ability of greases depend on both the base oil and the thickener. Mineral oils are the most widely used lubricant base fluids due to their inherent lubricity and low cost, but recent environmental awareness has forced consideration of the use of biodegradable fluids such as vegetable oils and certain synthetic fluids in grease formulations. This study presents data on the thermo-oxidation behavior and tribology of biodegradable greases formulated with soybean oil and different compositions of metal soap thickener. The composition of thickener has been varied by using fatty acids with different degrees of unsaturation and fatty acids of different chain lengths. The improvement of thermo-oxidation and tribological properties as a result of changing thickener/base oil ratio and the antioxidative effect of some suitable additives have also been evaluated.

KEYWORDS: Grease; soybean oil; vegetable oils; oxidative stability; friction

INTRODUCTION

Lubricating greases are colloidal dispersions of a thickener in a lubricating fluid and are generally formed by heating the two components together until the thickener swells and absorbs the oil. Grease is a preferred form of lubrication in certain applications because it gives low friction, is easily confined, and has a long lubricating life at low cost. A number of studies have been reported on various aspects of mineral oil based grease characterization to understand the fundamental aspects of grease lubrication, such as their structure (1–3), thermo-oxidative stability (4, 5), oxidative degradation using chromatographic and spectroscopic techniques (6), and grease lubrication mechanism of rolling element bearings (7). Sivik et al. (8) have discussed the possible grease interactions such as zinc dithiophosphate with lithium soap, oil with grease, and grease with metal surface. Silverstein and Rudnick (9) have described the main factors that affect grease properties and performance and also the design of cost-effective and environmentally friendly lubricant additive technologies for grease applications. The effect of grease fiber structure plays an important role in their frictional performance (10). It has been reported that in mixed and boundary lubrication regimes, the greases were superior in frictional performance compared to the base oil. Mistry and Bradbury (11) investigated the effect of solid additive concentrations in greases, so as to obtain optimum load/wear performance.

Environmentally friendly lubricants and greases are already on the market (12). These products are very desirable in total loss lubricants such as railroads, because their release does not cause any harm to the environment when it comes in contact with soil and water. Certain synthetic greases, which are based on low molecular weight poly(α -olefin), polyglycols, polyol esters, and diesters, are biodegradable and environmentally friendly, but their higher cost limits their applications only in niche areas such as aerospace, computer, and medical applications (13). However, vegetable oil based greases have poor thermo-oxidative stability and thus cannot be used at high temperatures. Dwivedi et al. (14) described the preparation of total vegetable oil based grease using castor oil. Florea et al. (15) have studied the effect of different base fluids on the properties of biodegradable greases. In most applications, a suitable composition of grease is desired with good performance properties capable of use in multifunctional products. Despite the overwhelming importance of biodegradable greases, very little is known about the relationship between their composition and performance properties (13). The thermo-oxidative stability of grease must be improved for use in various applications. This paper is an attempt to understand how the composition of thickeners in soy-based greases affects their thermo-oxidative stability and tribochemical properties and the effect of additive in obtaining longer life of vegetable oil based greases.

EXPERIMENTAL PROCEDURES

Greases. The base oil used in grease preparation was alkali refined soybean oil (Pioneer High Bred International Inc., Des Moines, IA). Properties of the soybean oil are given in **Table 1**. This oil shows much lower linolenic content (0.5%) than regular soybean oil ($\geq 8\%$). The

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Table 1. Soybean Oil Properties

property	SBO
density (g/mL)	0.914
kinematic viscosity at 40 °C, cSt (ASTM D445) ^a	32.4
kinematic viscosity at 100 °C, cSt (ASTM D445) ^a	8.08
viscosity index	225
pour point, °C (ASTM D97) ^a	-6
flash point, °C	254
acid value, mg of KOH/g (AOCS, Ca 5a-40) ^b	0.16
peroxide value, mequiv kg ⁻¹ (AOCS, Cd 8-53) ^b	9.76
iodine value, mg of I ₂ g ⁻¹ (AOCS, Cd 1-25) ^b	144.8
fatty acid composition by GC, % (AACC, 58-18) ^c	
C _{16:0}	6.0
C _{18:0}	5.5
C _{18:1}	22.0
C _{18:2}	66.0
C _{18:3}	0.5
onset temperature, PDSC, °C	178
biodegradability, % (CEC test)	98

^a Annual Book of ASTM Standards, 2000; Vol. 05.01. ^b Official Methods and Recommended Practices of the AOCS, 5th ed., 1998. ^c Approved Methods of the American Association of Cereal Chemists, 10th ed.; 2000; Vol. II.

lower linolenic acid moiety in the fatty acid chain results in a significant improvement in the thermo-oxidative stability of vegetable oil structure. Grease is constituted by 75–95% lubricating fluid, 5–20% thickeners, and the rest (1–10%) additives. Therefore, the biodegradability of grease depends a lot on fluids and thickeners. The soybean oil (SBO) used in this study as lubricating base fluid is rapidly biodegradable (Table 1), and the thickeners such as lithium soaps are not considered to be harmful to the environment. The biodegradability (CEC L-33-A-93 test) of soybean oil is 98% compared to 20–40% for super-refined mineral oils (16), 20–80% for poly(α -olefins), 50–100% for diesters, 15–65% for polymer esters, and 10–70% for poly(ethylene glycol)s (17). Similarly, the biodegradability of vegetable oil based greases is >85% (15) compared to 14% of mineral oil based grease.

Lithium hydroxide monohydrate (LiOH·H₂O, 98%) and palmitic (96.8%), stearic (97.6%), oleic (94%), and linoleic acids (90%) were obtained from Aldrich Chemical Co. (Milwaukee, WI) and were used without any further purification. A commercial antimony dithiocarbamate additive package (R. T. Vanderbilt Co., Norwalk, CT) was used for this study. This additive functions both as an antioxidant and an extreme pressure agent. Additive concentrations were varied using 2 or 4 wt % in different grease formulations.

A mixture of LiOH·H₂O, fatty acid (1:1 equivalent ratio), and soybean oil (in equivalent weight ratio of the metal–acid mixture) was uniformly mixed with a mechanical stirrer at 90 °C in a 3-L, wide-mouth glass reactor. The temperature was then slowly raised to 190 ± 2 °C and maintained for 3 h with stirring. The mixture was then allowed to cool, and at 150 °C additional amounts of SBO (60–80% of the total reaction mixture) and additive (0–4 wt % of the total reaction mixture) were added. The final mixture was allowed to cool to room temperature to obtain the grease. The resulting grease was passed through a three-roller mill (model 49095, Kent Machine Works, Brooklyn, NY) to homogenize it. A similar procedure was used to prepare all of the other greases (Table 2) with varying composition in soap/oil ratio, unsaturation, chain length of fatty acids (FA), and additive concentration (18, 19). The ratio of lithium soap of different fatty acids and soybean oil is 1:3 in all greases except GR11 with 1:2 and GR28 with 1:4. The greases GR11, GR12, and GR28 have soap/oil ratios of 1:2, 1:3, and 1:4, respectively. There are three greases, GR5, GR12, and GR27, in which soaps are prepared with lithium hydroxide monohydrate and fatty acids with different degrees of unsaturation, 0 (stearic), 1 (oleic), and 2 (linoleic), respectively. The chain length effect of fatty acids used in the preparation of soaps is studied with greases GR9, GR24, GR7, and GR5 having C₁₂ (lauric), C₁₄ (myristic), C₁₆ (palmitic), and C₁₈ (stearic) carbon chains, respectively. The concentration of antimony dithiocarbamate is varied in greases GR5 with 0%, GR13 with 2%, and GR25 with 4% to study the additive effect. NLGI (National Lubricating Grease Institute) hardness of greases was determined as per ASTM D 217 (20).

Table 2. Greases with Variation in Their Composition

grease	thickener	thickener/ oil ^a	additive ^b amount, %	NLGI hardness ^c	CoF ^d
soap/oil ratio					
GR11 (1:2)	lithium oleate (C _{18:1})	1:2		4	0.363
GR12 (1:3)	lithium oleate (C _{18:1})	1:3		2–3	0.281
GR28 (1:4)	lithium oleate (C _{18:1})	1:4		2	0.215
unsaturation					
GR5 (0)	lithium stearate (C _{18:0})	1:3		2–3	0.237
GR12 (1)	lithium oleate (C _{18:1})	1:3		2–3	0.281
GR27 (2)	lithium linoleate (C _{18:2})	1:3		1	0.298
chain length					
GR9 (12)	lithium laurate (C ₁₂)	1:3		0	0.139
GR24 (14)	lithium myristate (C ₁₄)	1:3		0	0.152
GR7 (16)	lithium palmitate (C ₁₆)	1:3		2	0.144
GR5 (18)	lithium stearate (C _{18:0})	1:3		2–3	0.237
additive effect					
GR5 (0%)	lithium stearate (C _{18:0})	1:3	0	2–3	0.237
GR13 (2%)	lithium stearate (C _{18:0})	1:3	2	2	0.209
GR25 (4%)	lithium stearate (C _{18:0})	1:3	4	2–3	0.143

^a Ratio of lithium soap of different fatty acids and soybean oil; soap/oil ratio is 1:3 in all greases except GR11, with 1:2, and GR28, with 1:4. ^b Antimony dithiocarbamate. ^c ASTM D217 ^d Coefficient of friction determined using ball-on-disk configuration; average value of three independent experiments with standard deviation ± 0.02.

Thin Film Micro-oxidation (TFMO). Approximately 0.15–0.2 g of the grease sample was accurately weighed and spread on an activated low carbon steel catalyst surface to make a thin film on the metal. The sample was oxidized under a steady stream of dry air (20 cm³/min) in a bottomless glass reactor on a hot plate at constant preset temperature (100, 125, 150, 200, and 225 °C) for a period of 2 h. The greases were also oxidized at 150 °C for periods of 2, 4, 6, 8, and 24 h. The tests were terminated after the stipulated time; the coupon was cooled and weighed to determine percent weight loss (also termed volatile loss) (21).

To generate information regarding the repeatability of the TFMO test, the oxidation test at 150 °C was performed in quadruplicate for 2 h on grease samples, and a standard deviation of 0.08 was obtained. The coefficient of variation (CV) is 4.5, and the percent weight loss values vary within ±0.1 of the average. This CV value is well in agreement with the reported CV value (5.5%) in the literature (4) for NLGI grease samples on steel pans at 150 °C for 24 h. This shows that the data generated in this study are accurate and reliable.

Pressurized Differential Scanning Calorimetry (PDSC). The equipment used was a PC-based PDSC 2910 thermal analyzer from TA Instruments (New Castle, DE). Typically 1.5–2.0 mg of sample was oxidized in an open aluminum pan. The unit was pressurized to 300 psi (2100 kPa) with air. The system temperature was ramped at 40 °C/min from room temperature to 90 °C, equilibrated at this temperature, and kept isothermal until the appearance of peak. The oxidation induction time (OIT) of three grease samples containing additive was calculated by extrapolating the tangent drawn on the steepest slope of the corresponding exotherm to the baseline. OIT is defined as the time when additives no longer prevent oxidation and a rapid increase in the rate of oxidation is observed in the system.

High-Temperature Stability Tests. An oven test method was designed to study the long-term oxidative stability of grease samples. Typically 3–4 g of sample is weighed into an aluminum foil cup and placed in the oven preheated to 100 °C. The test samples are left in the oven, and the weight loss is recorded after 4, 23, 49, 73, 96, and 123 h. Higher weight loss indicates high volatility due to evaporation and low stability of the oil. After 123 h of oven oxidation, the oxidized grease samples were analyzed for their total acid number and changes in functional groups using FTIR. Infrared spectra were obtained with a thin film of sample between two KBr pellets using a Nicolet FTIR spectrometer at 4 cm⁻¹ resolution and 32 scans.

Rotary bomb oxidation tests (RBOT) were also carried out as per ASTM method D 942 (22) on one commercial mineral oil based grease

(NLGI1) and three biobased grease samples prepared in this study (GR5, GR13, and GR25).

Friction Measurement by Ball-on-Disk Method. Boundary lubrication properties of grease samples were studied using a multispecimen friction test apparatus from FALEX (Sugar Grove, IL). Ball-on-disk experiments were carried out at room temperature under low speed, 6.22 mm s^{-1} (5 rpm), and high load, 1778 N, using the grease samples. The test specimens were 1018 steel disks, Rc 15–25, and a ball (52100 steel, 12.7 mm diameter, 64–66 Rc hardness, and extreme polish). The coefficient of friction (CoF) values were measured and are reported as averages of two or three independent experiments in **Table 2**. The CoF values varied by ± 0.02 from the average.

RESULTS AND DISCUSSION

Soybean oil is the most widely used vegetable oil in biodegradable lubricant formulations and has the advantages of being a natural renewable resource and almost completely biodegradable. The structure of fatty acids of a vegetable oil determines the oxidation and lubrication properties of grease. Excess polyunsaturated fatty acids (FAs) impart unfavorable oxidation and chemical stability at high temperatures, whereas certain saturated FAs lead to poor low-temperature flow properties. The FAs used in the soap preparation also play an important role in grease manufacture; therefore, different FAs were used in soap preparation to study the difference in properties of the grease. All greases in this study were prepared using various lithium soaps (lithium stearate, oleate, linoleate, laurate, myristate, or palmitate) as described elsewhere (18). For vegetable oil based greases, a higher thickener content is required to give the same consistency (NLGI hardness) as that of conventional mineral oil based greases (15); therefore, the thickener-to-oil ratio is varied in this study to get the best properties with optimum thickener content. The physical properties of these greases are reported in a previous paper (18). The chemical and performance properties of these greases are presented in this paper.

Soap/Oil Ratio. Most lubricating conditions are thin film, so the TFMO test was conducted to simulate the actual conditions. The TFMO is a test of choice for quantitative evaluation of grease thermal and oxidative stabilities, because of its time-saving feature and its good correlation with the PDSC method and the time-consuming ASTM D 942 bomb oxidation test (4). The weight loss values obtained from TFMO at different temperatures and times at 150 °C are shown in **Figures 1** and **2**, respectively. Weight loss in vegetable oil based greases at 150 °C for 24 h is $\sim 10\%$, which is much lower compared to weight loss in mineral oil based greases ($\sim 50\%$) under similar conditions (4). The weight loss obtained from TFMO tests may be used to predict the useful life of grease, as it provides information about the amount of base fluid left in the grease for lubrication. The amount of oil left in the grease after TFMO is present in the form of unoxidized oil, polar oxidation products, and polymerized products. Panels **a–d** of **Figure 1** show that the rate of weight loss is almost constant from 100 to 150 °C and increases rapidly as the temperature is raised to 200 °C and then to 225 °C. This indicates that the breakdown of molecules present in soy-based greases as a result of oxidative degradation is more rapid after 150 °C.

The grease samples were synthesized with different soap/oil ratios to study the effect of the soap on oxidation stability and wear behavior. GR11 has a soap/oil ratio of 1:2, followed by GR12 with 1:3 and GR28 with 1:4. **Figure 1a** shows the weight loss in greases GR11, GR12, and GR28 during TFMO at temperatures ranging from 100 to 225 °C. The weight loss decreased with increasing oil ratio (or decreasing soap content)

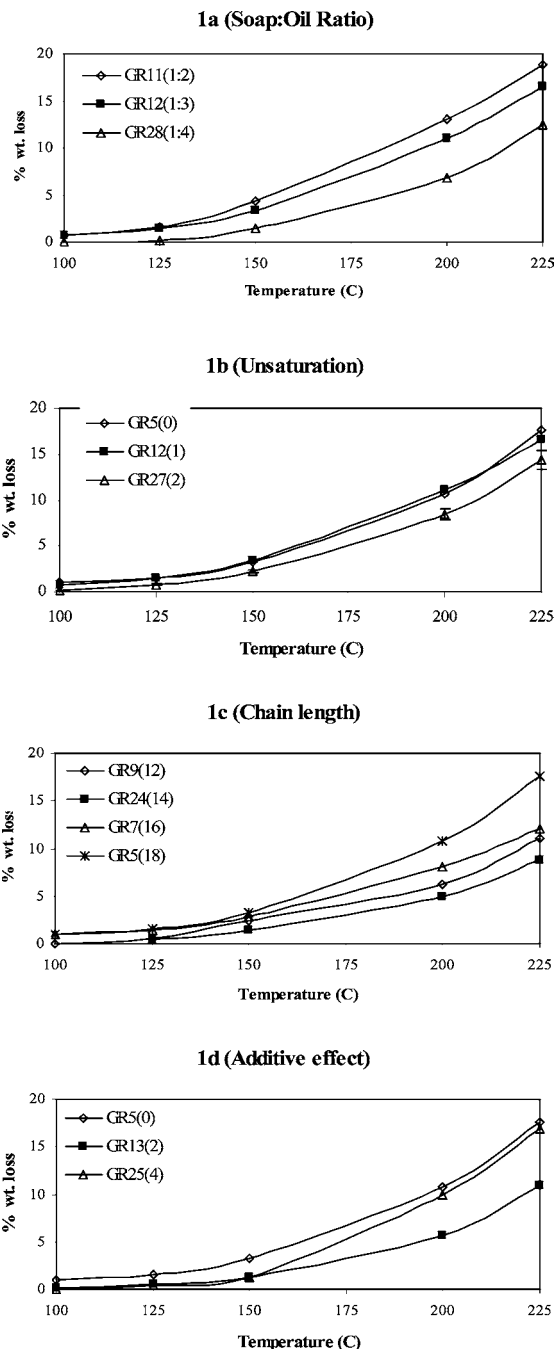


Figure 1. Compositional effects of grease at different temperatures using TFMO.

in greases. Similar results were found when the greases were oxidized at 150 °C for 2, 4, 6, 8, and 24 h (**Figure 2a**) and in the high-temperature and long-duration oven test, during which the grease samples were oxidized at 100 °C for up to 123 h (**Figure 3a**). After 123 h of oven oxidation, the total acid number (TAN) of GR28 is minimum (21.84 mg of KOH/g), followed by GR11 (23.93 mg of KOH/g) and GR12 (25.83 mg of KOH/g). This shows that the extent of oxidation is least in grease sample GR28. The appearance of all the greases (listed in **Table 2**) after the oven test changed to that of a rubber-like substance. In general, as the soap/oil ratio increases in greases, the oxidation stability also increases. The improved volatility characteristics of grease GR28 with a higher soap/oil ratio (1:4) are attributed to better interaction between soap fiber structure and the confined base oil. The fiber–base oil interaction profile of the grease matrix is not fully developed in GR11 (soap-to-oil ratio

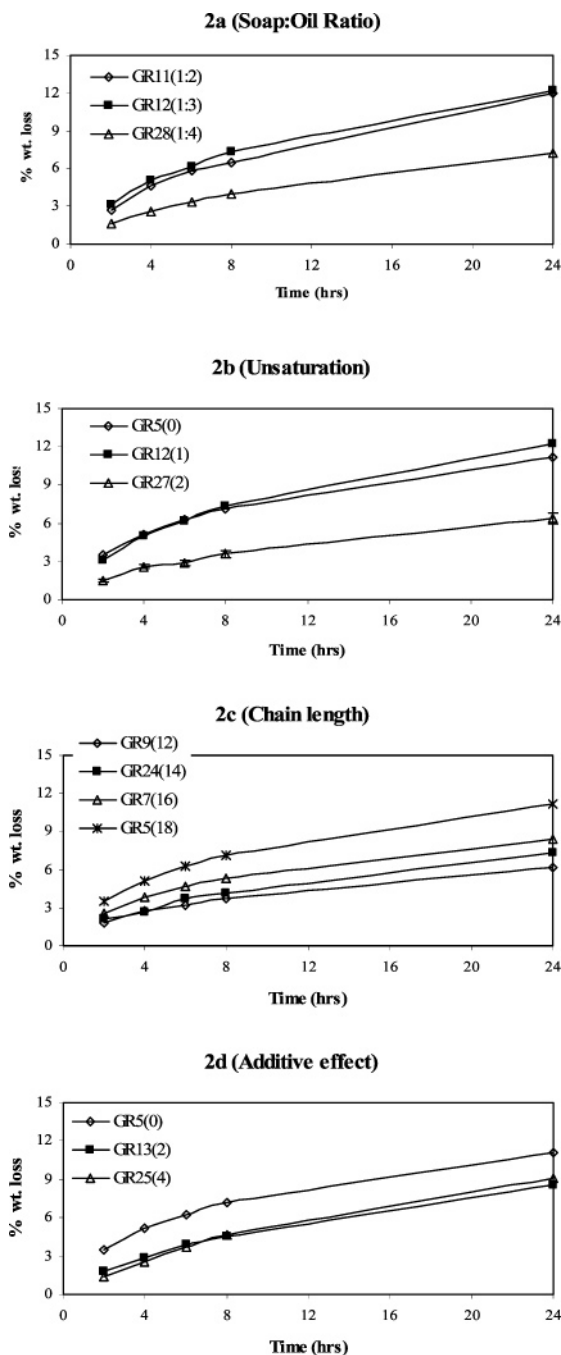


Figure 2. Grease compositional effects at 150 °C as a function of time using TFMO.

of 1:2) and therefore resulted in “bleeding” of the base oil at test temperatures. This oil is more amenable to oxidation and thermal evaporation loss compared to the oil confined in the grease matrix.

The development of lubricating grease with the right consistency requires stringent optimization of components and preparation protocol. Important performance properties such as adhesion, rheology, and lubrication are largely dependent on the grease hardness and its ability to maintain a stable lubricating film at the metal contact zone. Grease with increasing base oil content tends to be softer but yet must maintain a stable matrix. Data presented in **Table 2** show the lowest CoF when GR28 was used. Thus, soap with an oil ratio of 1:4 resulted in a soft grease (GR28, NLGI hardness 2) that was capable of better wetting the metal surface during the tribochemical process. Comparatively harder greases GR11 and GR12 (1:2 and 1:3

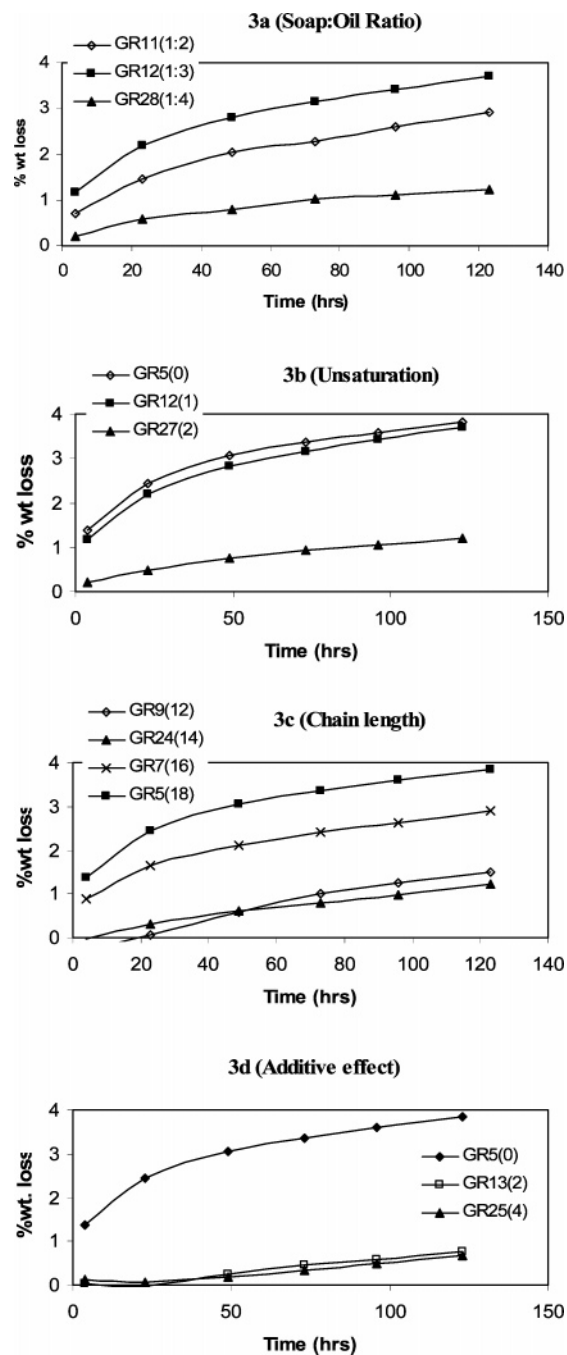


Figure 3. Weight loss obtained from oven test at 100 °C.

soap-to-oil ratios, respectively) under the given geometry of the wear test would be pushed to the side by the rotating ball and were unable to return to relubricate the metals in contact. This condition often leads to starved lubrication. GR11 and GR12 are NLGI 4 and 2–3, respectively.

Unsaturation. Lithium soaps were prepared with different fatty acids having varying degrees of unsaturation for use in soy-based greases: stearic ($C_{18:0}$) in GR5, oleic ($C_{18:1}$) in GR12, and linoleic ($C_{18:2}$) in GR27. Weight loss during TFMO as a function of temperature is shown in **Figure 1b** and as a function of time in **Figure 2b**. Overall, GR27 with lithium linoleate soap showed the least weight loss compared to GR12 with lithium oleate soap and GR5 with lithium stearate soap. Similar results were found in TFMO time-based study (**Figure 2b**). In this experiment, GR5 and GR12 showed higher weight loss compared to GR27 during the entire duration of oxidation. This observation was further supported by a long-term oxidation

stability oven test (**Figure 3b**). The total weight loss for GR27 is ~1%, whereas GR5 and GR12 show similar degradation kinetics with exactly overlapping weight loss patterns and maximum weight losses of ~4% reached after 123 h of oxidation (**Figure 3b**). The kinetics and mechanism of oxidative degradation for GR27 are different from those of GR5 and GR12. The greases GR5 (0) and GR12 (1) are very similar in their oxidation stabilities. The experimental data in **Figures 1b, 2b, and 3b** suggest that little benefit in weight loss is afforded by increasing the unsaturation from 0 to 1. However, increasing the unsaturation to 2 yields a reduction in the weight loss. The real effect of unsaturation is visible only when it is increased from 1 to 2. Unsaturation in the fatty acid structure of the soap molecule has a significant impact on the grease fiber structure. Lithium linoleate ($C_{18:2}$) with two sites of C–C unsaturation in the chain shows a much thinner and more compact fiber network than lithium oleate ($C_{18:1}$) and lithium stearate ($C_{18:0}$) in the soap composition. A compact soap fiber structure will result in greater interaction with the base oil. This phenomenon will translate into a low evaporation loss. During the oxidation process, primary oxidation products undergo further oxy-polymerization reaction in the presence of excess oxygen to form an oil-insoluble deposit (23). The presence of more double bonds in the fatty acid structure of soap are attractive sites for reaction with primary oxidation products, which results in more polymerization (leading to grease hardening) and less volatile oxidation product formation. It is likely that GR27 (two double bonds) may undergo rapid oxidative polymerization of the grease that will lead to less volatile product formation. This is further supported by TAN values of greases oxidized in an oven for 123 h. More oxidation in GR27 and GR12 has resulted in comparatively higher TAN values (25.6 and 25.83 mg of KOH/g, respectively) compared to GR5 (24.7 mg of KOH/g).

There was no major difference in the CoF as a result of change in the fatty acid unsaturation in the Li soap structure. However, results indicate a small increase in the friction coefficient with increasing unsaturation. GR5 is lower in friction coefficient than GR12, which is only slightly lower than GR27.

Chain Length of FA. The effect of hydrocarbon chain length on the oxidative stability of greases was evaluated using a series of lithium-based soaps prepared with fatty acids having different chain lengths. Greases GR9 with lithium laurate soap (C_{12}), GR24 with lithium myristate (C_{14}), GR7 with lithium palmitate (C_{16}), and GR5 with lithium stearate (C_{18}) were prepared under identical conditions and compositions. The TFMO degradation pattern is shown with varying temperature (**Figure 1c**) and time (**Figure 2c**). The weight loss increases with increasing molecular weight of the soap or increasing chain length of FAs used in soap preparation. The weight loss is maximum in grease GR5 (C_{18}) followed by GR7 (C_{16}) and lowest for GR9 (C_{12}). A similar trend was obtained when the TFMO experiment was performed at 150 °C within the time range of 2–24 h (**Figure 2c**) and in an extended period oven test with minimum in GR9 (C_{12} FA) and GR24 (C_{14} FA), more in GR7 (C_{16} FA), and maximum in GR5 lithium stearate (C_{18}) soap (**Figure 3c**). The weight loss trend obtained in the oven test exactly coincides with TAN values of greases oxidized in an oven at 100 °C for 123 h. The TAN value is maximum in grease GR5 (24.7 mg of KOH/g) followed by GR7 (16.22 mg of KOH/g) and minimum in GR9 (15.04 mg of KOH/g) and GR24 (14.39 mg of KOH/g). These results further support the data obtained from TFMO experiments. Overall, the percent weight loss as well as TAN values increases with increasing FA chain lengths used in the Li soap as in **Figure 2c**. Although the effect of chain length is less

marked in **Figures 1c and 3c** for greases GR9 and GR24 with lower chain lengths C_{12} and C_{14} , respectively, it is very clear in **Figure 2c**. The possible reason is the mild oxidation conditions used in **Figure 2c**, but in harsh conditions, such as increased temperature (**Figure 1c**) or extended period of time (**Figure 3c**), it is difficult to distinguish between greases made from soaps having lower chain length FAs. The overall trend from the effect of fatty acid chain length can be explained by the stability of the grease thickener. Grease subjected to high-temperature oxidation for an extended time period will result in the destruction of thickener structure, leading to much weaker and thinner fibers. This process will lead to grease softening (decrease in consistency or NLGI hardness) resulting in base oil bleeding from the grease matrix. Lowering the ratio of fiber length L to width D , L/D , results in softer grease. As soon as the base fluid is released from the soap structure, it is subjected to high temperature and thus susceptible to oxidation, leading to greater volatile loss. Lithium soaps of FAs leading to short and thick fiber structures are relatively stable to thermal breakdown and, therefore, evaporation loss during extended time oxidation is low. This observation is supported in another study (24), wherein they mentioned that short-chain acids are more stable than long.

Lubricating properties of grease depend to a large extent on the grease consistency resulting from the soap thickener microstructure. Increasing the FA chain length in soap resulted in stronger bonding interaction and therefore a harder grease matrix. Relatively softer grease has a better spreading tendency and metal adhesion possibility and eliminates conditions such as starved lubrication. A significant amount of grease is removed from the friction zone due to plowing. If grease containing the base oil is unable to relubricate before the second pass, this will significantly increase the friction between the metals in contact. Friction data from ball-on-disk geometry (**Table 2**) for GR9, GR24, GR7, and GR5 with increasing chain length of Li soap FAs resulted in increasing friction coefficients when the corresponding grease was used. This is contrary to other studies in which the CoF decreases with increasing chain length. It appears that the grease consistency and its ability to maintain the lubricant in the contact zone are the predominant factors. A trade-off has to be reached in developing grease with desired consistency that will also deliver optimum friction properties.

Additive Effects. The oxidation stability of biobased greases can be improved by using suitable antioxidant (AO) additives in optimized concentration. Generally a higher concentration of additives is necessary in biobased formulations to attain properties similar to those of mineral oil based greases (15). Grease GR5 contains no additive (unadditivated grease), whereas greases GR13 and GR25 contain 2 and 4% AO additive, respectively. The effect of antioxidant in grease formulation is clearly observed from the TFMO data at different temperatures (**Figure 1d**). The oxidation onset temperature for additivated samples GR13 and GR25 is much higher (150 °C) compared to unadditivated sample GR5 (<100 °C). **Figure 2d** shows the measured weight loss of greases with time in the TFMO experiment at 150 °C. All three greases show progressive increase in weight loss with time. There is a decrease in measured weight loss with increasing additive concentration. Unadditivated grease (GR5) shows higher weight loss compared to additivated greases (GR13 and GR25). The two greases GR13 and GR25 (with additive) show similar degradation behaviors, and there is no apparent difference in their weight losses at different times. The same trend was observed in the extended period thermal stability test (oven test) at 100 °C, where a clear

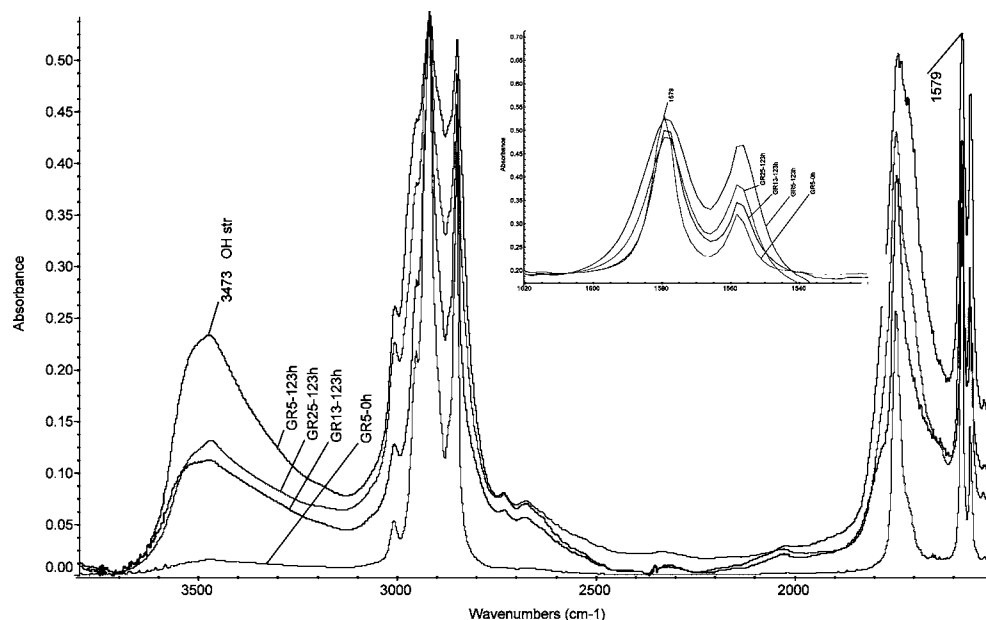


Figure 4. FTIR spectra of grease GR5 before test (GR5-0h) and GR5, GR13, and GR25 after 123 h in oven test at 100 °C.

difference is observed in unadditivated (GR5) and additivated (GR13 and GR25) greases (**Figure 3d**). Results indicate GR5 to be unstable with a maximum weight loss of $\sim 4\%$ at 123 h, whereas GR13 and GR25 are exceptionally stable greases ($\sim 0.7\%$ loss after 123 h). Significant oxidative degradation was observed for GR5 (no additive) immediately after the start of experiment, whereas GR13 and GR25 both have induction times of 23 h for oxidation to start (**Figure 3d**). Even after 23 h, the oxidative degradation is very slow in GR13 and GR25, whereas it is much faster in GR5. The different trends of decrease in the weight of unadditivated and additivated greases show that this is the result of oxidative degradation and not due to evaporation loss of the base oils, as all three have similar base oils. The oxidative degradation mechanism has changed completely in the presence of the additive, which is acting by inhibiting the oxidation. Therefore, the presence of additive in the grease formulation has a significant effect on the thermo-oxidative stability and consequent weight loss during extended time high-temperature applications. **Figure 4** shows the FTIR spectra of grease GR5 before the test and greases GR5, GR13, and GR25 after oxidizing in the oven at 100 °C for 123 h. The absorption at 1579 cm^{-1} caused by the thickener (25) was not changed in additivated and unadditivated greases. This shows that the thickener (lithium stearate) of all three greases did not deteriorate during the test and is stable at 100 °C. On the other hand, the absorption at 3473 cm^{-1} , which is due to a hydrogen-bonded OH group, was stronger in the unadditivated grease after the oven test (GR5-123h) compared to additivated greases after the oven test (GR13-123h and GR25-123h) and least in unadditivated grease before the oven test (GR5-0h). The oxidation of base oil present in the grease occurs during thermal aging and results in the formation of organic acids as byproducts. The presence of these organic acids in the oxidized grease samples (GR5-123h) is visible from the broad hump in the region $3100\text{--}2500\text{ cm}^{-1}$ and also from the peak shoulders at 1717 and 1700 cm^{-1} , which is due to the carbonyl group of acid byproducts (5). The presence of additive in GR13 and GR25 delayed the oxidation process as shown by lesser OH absorption and acid byproducts in these greases. These organic acids accelerate the increase of weight loss and the viscosity of the base oil, resulting in harder grease. The formation of acid byproducts has been confirmed by TAN values obtained for

greases oxidized in the oven at 100 °C for 123 h. The TAN value of virgin grease GR5 is 14.59 mg of KOH/g, and it corresponds to a very small hump in the IR spectral region ($3700\text{--}2500\text{ cm}^{-1}$) of GR5-0h, and after 123 h of oxidation in the oven test, it has increased to 24.7 mg of KOH/g corresponding to a big peak and big hump in a similar spectral region for GR5-123h, showing the formation of acid byproduct during oxidation. The grease with 2% additive, GR13, shows a TAN value of 10.97 mg of KOH/g, and the grease with 4% additive, GR25, has a TAN value of 17.55 mg of KOH/g after 123 h of oven oxidation. These TAN values vary in a similar way to the peak intensity of IR peak 3473 cm^{-1} shown in **Figure 4**. By adding this additive, the increase of TAN value was delayed in GR13. It may be concluded that during the oven test, thickeners in these greases remain unchanged, whereas the vegetable oil is oxidized and polymerized, resulting in a rubber-like appearance and hardening of grease. The thermo-oxidative study using TFMO may correlate more readily with various high-temperature bearing tests. Oxidation in the TFMO test occurs on a metal surface in an open atmosphere where evaporation can occur. Therefore, TFMO may be used as a grease development and specification tool for grease applications in specific operating conditions and component metallurgy.

The oxidation stability of grease samples (GR5, GR13, and GR25) was also studied by RBOT, wherein the pressure drop in the bomb was recorded with time. The RBOT results of soy-based greases are shown along with those of mineral oil based NLGI-1 grease, as standard (**Figure 5**). No apparent pressure drop was observed in NLGI-1, showing extremely high oxidation stability for this sample. The oxidation behavior of GR25 (4% antioxidant) was similar to that of NLGI grease up to ~ 150 min with no pressure drop, and thereafter, the pressure started dropping as the onset of oxidation resulted in the consumption of oxygen in the bomb. The onset time for oxidation to start in GR25 is ~ 150 min, which also signals the depletion of antioxidant. GR13 (2% antioxidant) has a lesser onset time (~ 80 min) compared to GR25. There was no significant oxidation or pressure drop until 80 min into the test for GR13 and GR25. However, the bomb pressure immediately started dropping for grease GR5, which contained no additive. The pressure decrease at the end of 242 min is maximum in GR5 (32.9 psi) followed by GR13 (31.7 psi) and least in GR25 (24.9 psi). A larger

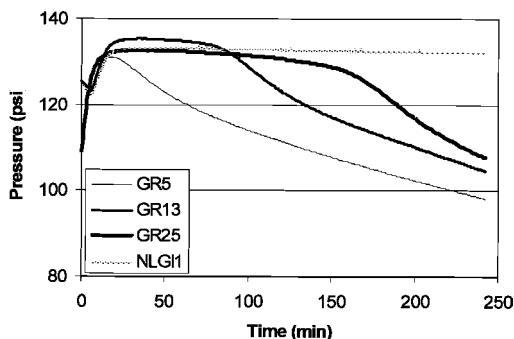


Figure 5. Compositional effects of grease in rotary bomb oxidation test.

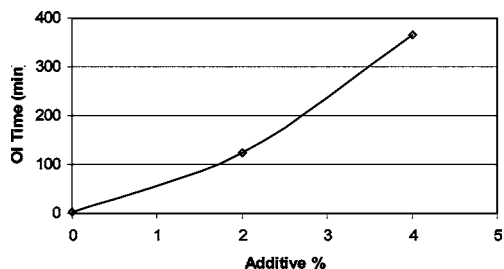


Figure 6. Effect of antioxidant concentration on PDSC oxidation induction times.

decrease in pressure drop was observed when the antioxidant concentration was increased from 2 to 4% than when it was increased from 0 to 2%.

PDSC is a faster way of measuring the oxidation characteristics of vegetable oil based greases. It is an effective way to study the antioxidant strength of an additive in grease formulation. The advantages of using high pressure in DSC are described elsewhere (23). The oxidation induction times (OIT) of GR5 (with no additive), GR13 (2% AO additive), and GR25 (4% AO additive) are shown in Figure 6. GR25 shows high oxidative stability (OIT = 366 min) followed by GR13 (124 min) and GR5 (3 min). The trend is in agreement with the RBOT results (Figure 5). PDSC is thus an effective tool to optimize additive concentration in vegetable oil based greases and for rapid assay of their thermal and oxidation behaviors.

The active component of the additive does not generally have chemical interaction with the Li soap or base oil. They are primarily dispersed in the oil in the grease matrix and start acting during the metal-rubbing process. During this time, additive molecules undergo chemical transformation at the metal contact zone and develop a stable tribochemical film to protect against further wear of the metal. The presence of additive in grease indicates a lowering of friction coefficient using a ball-on-disk test geometry. Higher additive concentration results in lower CoF of the corresponding grease (Table 2), showing that GR25 with 4% additive will have longest grease life followed by GR13 with 2% and GR5 without additives. Further increase in the additive concentration shows significant improvement in friction behavior. This is because the polar vegetable oils and additives compete for the metal surfaces, and a higher proportion of additive will increase its rate of diffusion to the metal surface.

In soybean oil based greases, the weight loss obtained during TFMO experiments is much lower compared to those of standard NLGI mineral oil based greases. Dholakia et al. (26) reported a weight loss of 20.5% for NLGI standard mineral oil based grease at 175 °C for 2 h, whereas soybean oil based additivated greases (GR13 and GR25) show a maximum weight loss of 5%. In another study by Harris et al. (4), the weight loss obtained in the TFMO test for NLGI mineral oil based

grease is 50% compared to 9% for soybean oil based grease GR25 at 150 °C for 24 h in steel pans. Higher evaporation losses in mineral oil based greases compared to vegetable oil based greases lead to increases in viscosity of the base oil present in the grease matrix and result in harder greases after oxidation. Similarly, weight loss in the oven test for the GR13 soybean oil based additivated grease at 100 °C for 49 h in aluminum pans is 0.23% and is comparable to a value of 0.36% for soybean oil based additivated grease (using lithium hydroxystearate as thickener) at 100 °C for 30 h in glass vessels, reported by Florea et al. (15). This shows that vegetable oil based greases prepared in this study are equally stable and that the data obtained are accurate.

This study offers insight about the thermo-oxidative and tribochemical behavior of vegetable oil based greases. The properties of grease depend not only on the base oil but also on the thickener composition. It has been shown in this study that thickeners have different influences on the properties of grease formulations, if the same base oil is used in all formulations. The following important inferences can be drawn from the above study on the thermo-oxidative stability of vegetable oil based greases.

- A high soap-to-oil ratio (within the range of 1:2 to 1:4) results in increased oxidation stability and lubricity of greases.
- A decrease in unsaturation in FA chains of soap molecules results in increased volatile loss as a result of the oxidative degradation of greases. Lubricity of greases decreased with more unsaturation in FA chains of soap molecules.
- The oxidation stability and lubricity of grease decrease with increasing FA chain length (within the range of 12–18) in soap molecules.
- The thermo-oxidative stability and lubricity of soybean oil based greases can be improved by using suitable additives.

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