Utilization of Olive-Residue Oil in the Formulation of Lubricating Calcium Greases

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ABSTRACT: Calcium greases were manufactured from olive-residue oil in a closed reactor by substituting olive-residue oil for animal tallow. The results of the performance tests applied to the obtained greases showed that their physicochemical and mechanical characteristics are comparable to those of calcium grease manufactured industrially by using animal tallow. The substitution of part of the animal tallow with olive-residue oil increased the thermal and mechanical stability of the grease. Olive-residue oil could constitute, alone or in combination with animal tallow, a raw material in the formulation of lubricating calcium grease.

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KEY WORDS: Animal tallow, calcium lubricating greases, mineral oils, olive-residue oil.

Lubricating grease is a semisolid product resulting from the fine dispersion of a thickening agent in lubricating oil (1). The thickening agent is generally a metallic soap prepared by saponification of a fatty substance.

Calcium greases manufactured in the lubricants industry in Tunisia are thickened by calcium soaps. The industrial manufacture of these greases uses animal tallow and calcium hydroxide as reagents for the preparation of the calcium soap. This reaction is conducted in a contactor, using a lubricating oil medium and in the presence of small quantities of water. The pressure caused by water vaporization and rapid agitation considerably reduces the time needed for saponification. The pressure also reduces the possibility of foaming (2).

The use of vegetable oils for the formulation of calcium greases has not been studied. Olive-residue oil is the main by-product of the olive oil industry. It is extracted, by organic solvents, from olive residue remaining after the grinding of olives and extraction of olive oil. This oil remains badly valorized because of its strong degradation and its very high acidity, generally exceeding 50% in mass.

Several methods have been developed to enhance the value of degraded vegetable oils, for example, by chemical refining with soda (3) and physical refining based on distillation (4). Distillation is certainly a very effective method of neutralization for vegetable oils with very high acidity, but it is very expensive in terms of energy consumption. Chemical neutralization with the soda used in the refining of edible oils makes it possible to separate the FA in the form of soaps. The slightly hydrated calcium hydroxide, used as a neutralizing agent in a biphasic liquid/solid medium, makes it possible to treat vegetable oils having very high acidity (5).

Other treatments of vegetable oils with high acidity have been proposed, most recently by esterification *in situ* of the FFA by a light monoalcohol or glycerol in the presence of mineral acids (5) or by ion exchange resins used as catalysts (6,7).

We propose in this work to develop a new method to enhance the value of olive-residue oil. This method consists in partially or completely substituting olive-residue oil for animal tallow in the formulation of lubricating calcium greases.

EXPERIMENTAL PROCEDURES

Chemicals. The olive-residue oil was provided by Sioszitex Company (Sfax, Tunisia). The used lime contained 90% by mass of calcium hydroxide, $Ca(OH)_2$. The lubricating oil was a blend of two mineral base oils (150 N and 600 N). The physicochemical characteristics of these base oils were measured by Sotulub (Bizerte, Tunisia) and are given in Table 1. Animal tallow was provided by Sotulub. All the other reagents and solvents were of analytical quality (Chemi Pharma, Tunis, Tunisia; Prolabo, Fontenay-sous-Bois, France).

Methods. (i) Physicochemical analyses of the fatty substances. To characterize the fatty substances used in this work, we carried out the following analyses: Titratable acidity (8) was based on a volumetric titration of the free acidity by a 7.1 g/L aqueous solution of sodium hydroxide. Saponification value (9) was determined by saponifying a specimen of fatty substance (2 g) for 1 h with a solution of potassium hydroxide in the ethanol. The excess of KOH was dosed with a 0.5 M solution of HCl to deduce the mass of KOH necessary to saponify 1 g of fatty substance. For iodine value (10), a specimen of fatty

TABLE 1
Physicochemical Characteristics[a] of Mineral Oils Used

Test	ASTM[b] method	Mineral oils 150 N	600 N
Carbon residue (%)	ASTM D-189	0.04	0.20
Pour point (°C)	ASTM D-2500	−4	−1
Flash point (°C)	ASTM D-92	204	246
Viscosity at 40°C (cSt)	ASTM D-445	29–31	109–116
Viscosity index[c]	ASTM D-2270	95	90

[a] Mean of two replicates. SD were 7–10%.
[b] ASTM, American Standards for Testing and Materials.
[c] Viscosity index is a number that indicates the effect of temperature changes on the viscosity of oil.

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*To whom correspondence should be addressed at Laboratory of Applied Chemistry: Heterocycles, Fats and Polymers, Faculté des Sciences de Sfax, Route de Soukra, Km 3,5–3018 Sfax, Tunisia. E-mail: Mah.Trabelsi@fss.rnu.tn substance was dissolved in 20 mL of CCl_4, and 25 mL of Wijs reagent (containing ICl) was added. The reaction occurred in darkness for 1 h to saturate all the double bonds of the fatty substance. After this time, 20 mL of KI solution and 100 mL of water were added. Liberated iodine was titrated by a 0.1 N solution of sodium thiosulfate to deduce the quantity of iodine fixed by the fatty substance. To determine unsaponifiable matter (11), a specimen of fatty substance (5 g) was saponified by 50 mL of a solution of KOH in ethanol. Unsaponifiables were extracted, by hexane, from the soapy solution, dried, and weighed to deduce the amount of unsaponifiable matter.

The FA composition of these substances was measured, as FAME, with a Trio 1000 (Fisons, Manchester, England) gas chromatograph–mass spectrometer (12). The capillary column was of CARBOWAX type with a length of 20 m, and the carrier gas was helium. The column temperature was held at 60°C for 10 min and then increased at a rate of 10°C/min to 300°C. The eluted FAME were identified by MS.

(ii) Preparation of lubricating greases. Lubricating greases were prepared in a contactor equipped with a mechanical agitator equipped with blades. A manometer measured the pressure inside the contactor. The fatty substance, lubricating oil, lime, and water were charged in the contactor. The presence of a lime excess, compared with the mass of lime calculated from the saponification value of the fatty substance, equal to 10% was set according to the industrial process. The compositions of the greases produced are given in Table 2.

The contactor was gradually heated to the desired temperature, under mechanical agitation. Greases **1**, **2**, and **3** were prepared, respectively, at 150°C for 90 min, at 120°C for 60 min, and at 120°C for 90 min. After cooling, specific additives were added to the product to improve some of its intrinsic properties (1). Among these additives were antioxidant agents, rust inhibitors, and antiwear agents. Greases were homogenized by milling.

(iii) Properties of the prepared greases. The greases produced were analyzed to determine their physicochemical characteristics and to evaluate their mechanical performances. Their characteristics were then compared to those of industrial calcium grease produced by Sotulub. The following analyses were carried out.

Dropping point (13) was determined with an apparatus consisting of a chromium-plated brass grease cup with a small opening at the bottom; a test tube of heat-resistant glass, with rim, 100–103 mm in length and 11.1–12.7 mm in i.d. in which the grease cup was placed; and an oil bath, consisting of a 400-mL beaker. Two thermometers, having temperature ranges from −5 to 300°C, were placed, one in the test tube and the other in the oil bath. The oil bath, containing the test tube, was gradually heated at a rate of 4 to 7°C/min. As the temperature increased, material protruded through the orifice of the grease cup. When a drop of grease fell, the temperatures on the two thermometers were noted and their average was taken as the dropping point of the grease.

TABLE 2
Compositions of Produced Greases

	Mass percentage		
Constituent	Grease **1**	Grease **2**	Grease **3**
Lubricating oil	75.6	70.0	73.2
Animal tallow	17.7	0.0	9.9
Olive-residue oil	0.0	22.7	9.9
Lime	3.0	3.4	3.1
Additives	2.4	3.0	2.7
Water	1.3	0.9	1.2

To determine shear stability (14), a penetrometer measured, in tenths of a millimeter, the depth to which the standard cone penetrated the grease. The sample of grease was subjected to 60 double strokes with a mechanical grease worker, a machine designed to operate the plunger of the grease worker mechanically. This apparatus was essential for the measurement of prolonged worked penetration (100,000 double strokes).

Oil separation (15) was determined with an assembled apparatus consisting of a tightly fitting cup and cover that contained a 75-µm (no. 200) sieve strainer for supporting the grease, a funnel for collecting the separated oil, and a 20-mL beaker for retaining the separated oil.

In the Schell roller test (16), the grease was laminated between two rollers at 25°C for 2 h. The penetration (P) was then measured and compared with the penetration after 60 double strokes of working. The result of the test was expressed by $\Delta = P -$ worked penetration (60 strokes).

In measuring corrosion (17), a copper strip was introduced in a beaker containing the grease tested. The beaker was then placed in an oven at 50°C for 48 h. The strip was then cleaned and compared, according to the final color, to ASTM standard strips identified by numbers and letters (1a, 1b, 2a, 2b, etc.). For example, strip no. 1a was slightly orange and strip no. 1b was dark orange.

In the water washout test (18), the assembled apparatus consisted of a ball bearing, a bearing housing, a water reservoir, a fluid pump, and a thermostated heater to heat water up to 79°C.

RESULTS AND DISCUSSION

Physicochemical analyses of the fatty substances. The quantity of calcium hydroxide necessary to saponify animal tallow or the olive-residue oil was determined by measuring the acidity and the saponification value of these fatty substances. Table 3 gives the chemical characteristics of animal tallow and those of the olive-residue oil.

The olive-residue oil had a very high acidity, thus verifying its degradation. The iodine value of this oil was 95.0, a value close to that of oleic acid (4). On the other hand, animal tallow had a low acidity and a relatively low iodine value. Thus, animal tallow was richer in saturated FA than olive-residue oil. GC–MS analysis of methyl esters of the two fats confirmed these results, as shown in Table 4. The olive-residue oil was mainly composed of oleic acid ($C_{18:1}$), a monounsaturated FA, whereas the animal tallow was mainly composed of saturated fatty acids ($C_{14:0}$, $C_{16:0}$, and $C_{18:0}$), but had

TABLE 3
Chemical Characteristics[a] of the Fatty Substances

Analysis	Olive-residue oil	Animal tallow
Acidity (mass %)	59.3	4.5
Saponification value (mg of KOH/1 g of fatty substance)	188.1	207.9
Iodine value (g of iodine/100 g of fatty substance)	95.0	38.0
Amount of unsaponifiable matter (mass %)	1.8	4.3

[a] Mean from three replicates.

TABLE 4
FA Compositions of Animal Tallow and Olive-Residue Oil

	Mass percentage	
FA	Animal tallow	Olive-residue oil
$C_{14:0}$	1.00	0.00
$C_{16:0}$	26.70	11.59
$C_{16:1}$	0.00	2.08
$C_{18:0}$	24.60	2.66
$C_{18:1}$	44.30	67.65
$C_{18:2}$	3.40	16.02

a relatively significant content of mono- and diunsaturated FA ($C_{18:1}$ and $C_{18:2}$). The two fatty substances were made up primarily of FA containing 18 carbon atoms.

Characterization of the finished greases. Physicochemical and mechanical testing methods were used on the finished greases to evaluate their performance. The results of the tests applied to our greases and commercial calcium grease (produced by Sotulub), denoted grease **4**, are shown in Table 5. The unworked penetrations (UnW.P) do not generally represent the consistency of greases in use as effectively as do worked penetrations (W.P). The values of UnW.P varied from one grease to another (from 218×10^{-1} mm for grease **2** to 292×10^{-1} mm for grease **1**). This variation was related to the percentages of built-in mineral oil and the nature and the composition of the soaps.

W.P results may be used to establish the consistency of lubricating greases within the NLGI (National Lubricating Grease Institute) consistency numbers shown in Table 6 (14). The values of worked penetration after 60 strokes showed that greases **1**, **2**, **3**, and **4** had NLGI numbers of 1/2, 3, 2, and 2, respectively, all of which were within the specification limits of calcium greases. The changes in UnW.P results of a grease after working of 60 strokes ($\Delta_1 = \text{W.P}_{60} - \text{UnW.P}$) and in W.P results after prolonged working of 100,000 strokes ($\Delta_2 = \text{W.P}_{100,000} - \text{W.P}_{60}$) were believed to be a measure of its shear stability. The change in W.P of grease after rolling in the Schell roller test (Δ) was believed to be a measure of its mechanical stability at rolling. The lower the values of Δ_1, Δ_2, and Δ are, the better the mechanical stability is.

Grease **3** ($\Delta_1 = +7.0 \times 10^{-1}$ mm) had better stability to the mechanical working of 60 strokes than grease **1** ($\Delta_1 = +12.0 \times 10^{-1}$ mm) and grease **2** ($\Delta_1 = +15.0 \times 10^{-1}$ mm). Moreover, the stability of grease **3** was very close to that of the commercial grease **4** ($\Delta_1 = +6.0 \times 10^{-1}$ mm).

TABLE 5
Characteristics of Finished Greases

Test	Grease **1**[a]	Grease **2**[a]	Grease **3**[a]	Grease **4** (commercial calcium grease)	Calcium grease specifications[b]
Unworked penetration[c], UnW.P (mm × 10)	292	218	281	282	220–310
Worked penetration 60 strokes[c], W.P_{60} (mm × 10)	304	233	288	288	220–310
Worked penetration 100,000 strokes[c], $\text{W.P}_{100,000}$ (mm × 10)	295	278	301	317	—
$\Delta_2 = \text{W.P}_{100,000} - \text{W.P}_{60}$ (mm × 10)	−9.0	+45.0	+13.0	+29.0	≤45.0[d]
Dropping point[c] (°C)	105	110	115	103	>100
Oil separation[c], 24 h at 25°C (%)	0.3	1.6	1.0	<5.0	≤5.0
Δ: Schell roller test[c], 2 h at 25°C (mm × 10)	−6.0	+42.0	−16.5	+17.0	≤45.0[d]
Copper corrosion, 48 h at 50°C (color)	1b	1b	1b	1a	1a
Water washout[c] (% of loss at 79°C)	10.5	10.0	9.7	8.3	NR[e]

[a] For compositions of these greases see Table 2.
[b] Sotulub (Bizerte, Tunisia) specifications for calcium greases.
[c] Mean data of two replicates. SD were 7–10%.
[d] Sotulub specifications for lithium greases; these tests are not required for calcium greases.
[e] NR, not required for calcium greases.

The values of Δ_2 (Table 5) showed that greases **1**, **2**, and **3** had good shear stability when subjected to the mechanical working of 100,000 strokes, since all values were ≤45 (limiting value tolerated for lithium greases). Grease **3** ($\Delta_2 = +13.0 \times 10^{-1}$ mm) had good behavior at prolonged working, definitely better than grease **2** ($\Delta_2 = +45.0 \times 10^{-1}$ mm) and grease **4** ($\Delta_2 = +29.0 \times 10^{-1}$ mm), but lower than grease **1** ($\Delta_2 = -9.0 \times 10^{-1}$ mm).

Greases **1**, **2**, and **3** had good mechanical stability at rolling since the values found in the Schell roller test (Table 5) were ≤45 (limiting value tolerated for lithium greases). Grease **1** ($\Delta = -6.0 \times 10^{-1}$ mm) and grease **3** ($\Delta = -16.5 \times 10^{-1}$ mm) had better stability than the reference commercial grease **4** ($\Delta = +17.0 \times 10^{-1}$ mm).

Based on the results of the mechanical benchmarks, substitution for part of the animal tallow by olive-residue oil in grease **3** clearly increased its mechanical stability.

The oil separation test documents the tendency of a lubricating grease to separate during storage. The values found in this test showed that greases **1**, **2**, and **3** gave percentages of oil separation less than 5%, in conformity with the calcium grease specifications.

The dropping point is the temperature at which a grease passes from a semisolid state to the fluid state. This change in state is typical of greases containing soaps of conventional types as thickeners (15). The measurement of dropping point generally determines the thermal stability of a grease. The experimental results (Table 5) showed that greases **1**, **2**, and **3** had dropping points greater than 100°C, in conformity with the calcium grease specifications. We noted better thermal performance of greases **2** and **3**. They had, respectively, dropping points of 110 and 115°C, higher than those of grease **1** (105°C) and grease **4** (103°C).

The test of copper strip corrosion made it possible to evaluate the corrosivity of greases with respect to copper parts or copper alloys. The results found in this test (Table 5) showed that greases **1**, **2**, and **3** did not corrode copper parts, since the results approached that of ASTM strip no. 1 (17), with a dark orange color (1b).

The water washout test measured the percentage of grease ejected through a bearing under the action of a water jet at 79°C. Low values (in %) on this test indicate better resistance of the grease to water washout. Results obtained for greases **1**, **2**, and **3** in this test (Table 5) were comparable to those obtained for the commercial grease **4**, taken as reference.

In light of these results, the calcium greases prepared from the olive-residue oil (grease **2**) and from the mixture of animal tallow and olive-residue oil (grease **3**) had characteristics very close to those of the commercial calcium grease. We could thus consider using olive-residue oil to substitute completely or partially for animal tallow in the preparation of calcium grease.

TABLE 6
NLGI[a] Consistency Numbers of Lubricating Greases (14)

NLGI consistency number	Worked penetration range, 25°C (mm × 10)
000	445–475
00	400–430
0	355–385
1	310–340
1/2	295–310
2	265–295
3	220–250
4	175–205
5	130–160
6	85–115

[a] NLGI, National Lubricating Grease Institute.

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