Lubricating Greases From Olive Oil, Corn Oil and Palm Oil

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The goal of the present work was to develop new lubricating greases from renewable resources, using calcium stearate soap as thickener agent dispersed in corn, olive and palm oils. The effects that temperature (in range 20 °C -60 °C) and concentration of the thickener agent (in range of 10%-30% wt) on the rheological properties of these lubricating greases was studied. Also morphological and melting characterization was performed. Due to their consistency, rheological behaviour, stability, non-toxicity and waterproof properties, the greases can be used for lubrication purposes in milder conditions such as sealing greases for food equipment or for chassis lubrication.

Keywords: biodegradable grease; lubricating grease; vegetable oil; rheology

Lubricating greases can be defined as solid to semi-fluid products, dispersions of a thickening agent in a liquid lubricant, mineral or synthetic oil, and may also contain additives to upgrade some special properties [1]. Typical grease contains 70–95% base oil and 5–30% thickener agent. The thickener agent is usually a metal soap, such as fatty acid soap of lithium, calcium, sodium, aluminum or barium [2]. The thickener forms a network, which traps the oil and confers the appropriate rheological and tribological behavior to the grease [1].

In all lubricating greases, the base fluid represents the principal ingredient. All lubricating oils must have the ability to separate adjoining moving surfaces to prevent or at least to minimize wear [3, 4]. The base oils with the highest viscosities have the best performance at the low speed and the high loads, the lowest evaporation loss, the strongest adhesion and the best water or solvent resistance. In general, oils with kinematic viscosities between 15 and 1500 mm^2 s^{-1} at 40°C are used. The oils with the lowest viscosities and the best low-temperature properties are recommended for lowest operational temperatures at the highest speeds [5-7].

However, as operating conditions become more severe, the demands on the lubricant are greatly increased. In order to perform under more severe conditions and to improve the desired tribological properties, the lubricant is formulated using one or more additives [8-14]. On the other hand, due to the increasingly stringent environmental regulations, it is necessary to improve the greases ecological friendliness characteristics [15, 16]. This objective can be realized by avoiding the harmful synthetic additives in the greases composition, without compromising their tribological properties. Anandan et al. [17] demonstrated in their research that the tribological properties of additive tree calcium stearate greases without additives are comparable with those of lithium base commercial greases containing additives.

The main market for lubricating greases is the automotive market. The most common greases are the conventional lithium, the conventional calcium, and seldom the sodium greases for re-lubrication of trucks, construction, farming, and forestry equipment, and old-fashioned cars. Calcium greases are produced at temperatures in the range of 120 and 160°C and can be used at temperatures up to 120°C; when prepared from suitable base oils they are probably the best greases for low-temperature uses. Their dropping point is between 130 and 150°C, depending on the base oil and additives. This type of greases usually has very good water resistance, adhesive properties, corrosion resistance and oxidation stability. Greases for lubricating machines used in food processing or in drinking-water systems, in which incidental and unavoidable contact between food and lubricant can occur, must fulfill specific requirements relating to food legislation, human health protection, taste, and odor [5].

Researches concerning the effects of composition and texture of thickeners agents on the greases wear and friction properties have been reported in many studies [18-20]. These studies demonstrated that the grease composition and processing conditions have a great influence on their microstructure and rheology. Sanchez et al. [21], Martin-Alfonso et al. [22] investigated the influence of cellulosic derivatives concentration ratio on the rheological and mechanical properties of oleo gels formulated with castor oil and cellulosic derivatives as thickener agents potentially applicable as bio-lubricating greases. Franco et al. [23] proposed some exponential models to evaluate the influence of the cellulosic additives on both the consistency index and the linear viscoelastic plateau modulus of the lubricating greases. Nunez et al. [24] studied new green grease formulations with blends of methylated cellulose pulp and ethylated derivative as thickener agents and they found that formulations show good rheological properties and appropriate mechanical stability. Garcia-Zapateiro [25] studied the rheological behavior of lubricating greases manufactured from vegetable oils with renewable thickener agent such as chitosan and Kraft cellulose pulp. Every study mentioned above demonstrated the feasibility of lubricant manufacture using raw of biological origin.

In previous works, Sterpu et al. [26, 27] investigated the rheological behaviour of some additive-free calcium

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stearate lubricating greases. Based on this study, it has been observed that the additive-free lubricating greases prepared have a non-Newtonian behavior described by the power law model (Ostwald de Waele model) and also the greases present thixotropy. The apparent viscosity of these greases increases with the content of calcium soap in the base-oil.

Nowadays, the lubricating market is interested in new completely biodegradable products, or more environmentally acceptable than traditional lubricants, even though at a higher price [28]. Moreover, 100% biodegradable materials are necessary to cover some specific applications, i.e. lubrication in food production, aiming to prevent any type of contamination in the manufacture of the final product [29].

Because of increasingly stringent environmental regulations, most of the last years studies [30, 31] are mainly focused on the replacement of mineral oils by vegetable ones. Even the vegetable oils present poor oxidative stability, in comparison to some of the mineral oils, they have good lubricity and ability for adhering to metal surfaces, low volatility, small viscosity–temperature dependence and, of course, non-toxicity and high biodegradability [32-34].

Taking into account these considerations, the main goal of the present work was focused on the development of new renewable and biodegradable lubricating greases, using calcium stearate soap as thickener agents dispersed in vegetables oils like corn, olive and palm oils. The effects that temperature and concentration of the thickener agent exert on the microstructure and the rheological properties of the corresponding biolubricating greases have been analyzed.

Experimental part

Materials and methods

Materials

Three vegetable oils were selected for the preparation of lubricant greases : extra virgin olive oil (41.4 cSt at 40 ^{o}C, from Auchan Import-Export Roumanie SRL), unrefined corn oil (38.9 cSt at 40 ^{o}C, from SC MAN Ro SRL) and palm oil (43.4 cSt at 40 ^{o}C, from Premier Perena). Strearic acid for synthesis from Merck and double filtered hydrated lime-$Ca(OH)_2$- from Carpat Var SRL were used to prepare the soap dispersions in the oil. A paraffinic mineral oil (37.4 cSt at 40 ^{o}C, from Tunic Prod SRL) served for the preparation of the benchmark grease.

Preparation of the lubricant greases

The preparation of the lubricant greases was performed in an open vessel with a helix agitator provided by Petrotest, Germany, in batches of 0.500 kg. The oil, stearic acid and $Ca(OH)_2$ were loaded from the beginning. During the preparation of the grease, the soap was obtained by reaction between stearic acid and calcium hydroxide:

$$2\ CH_3\text{-}(CH_2)_{16}\text{-}COOH + Ca(OH)_2 \rightarrow (CH_3\text{-}\ (CH_2)_2\text{-}COO)_2Ca + 2\ H_2O.$$

The formed soap was dispersed in the oil, as microcrystals, singular or in a network.

The agitator worked at a variable rotation speed, increasing by the end of the preparation process for good mixing purposes. The temperature of the mixture was kept constant at 90 ^{o}C during the process and the preparation took an hour. At the end of the preparation, the mixture was cooled down by natural convection.

There were prepared 15 greases corresponding to soap concentrations of 10; 15; 20, 25 and 30% for each oil type. The benchmark grease was prepared from the mineral oil with 20% soap, in the same conditions and was characterized in a previous work [23].

Greases density determination at different temperatures

The density values were needed for the calculations related to the dynamic viscosity. This was a good opportunity to study the variation of greases density with temperature. The NYE CTM003 cup method for density and specific gravity of lubricating greases was adapted for determinations at higher temperatures than that specified in the NYE method (25^{o}C): 20; 30; 40; 50; 60^{o}C.

Morphological observations

Optical microscopy was used for morphological investigations on the sample prepared as is without any additional treatment. Small piece of about 3 mm^3 sample was place on clean microscope slide and cover glass was push from the top to disperse the sample on slide surface.

The optical microscope was BIOROM-T type with objectives having x4(NA=0.14), x10(NA=0.3), x16(NA=0.35) magnification factor, designed for 160 mm mechanical tube length. The images were capture with a color CCD camera Ikegami ICD-504P model, with additional 3.2x magnification factor, connected a frame grabber and Analysis 2.1 application for digital image acquisition.

ImageJ was used to measure length or diameter of particulate forms on the sample. Statistics of measurements was performed in SciDAVIS software, and lognormal distribution was assumed based on determined skewness and kurtosis parameter for each sample.

Rheological characterizatio*n*

The rheological characterization was carried out with a rheoscope Haake VT 550, Germany, having a plate-cone geometry. The Sensors System PK1 1.0^{o} No 31 contains a cone with a radius R_1 = 0.014 m and angle á= $1.74 \cdot 10^{-2}$ rad, with a gap between the cone and the plate of $5 \cdot 10^{-5}$ m.

The samples were characterized at temperatures between 20 and 60 ^{o}C, both with increasing and decreasing shear rate, in range of 9.97 – 4500 s^{-1}, corresponding to 2 - 964 rotations per minute, for the given geometry of the rheoscope.

The reports containing the variation of shear stress with shear rate were provided by the software included in the rheological system. Every variation curve was built in 100 points.

Dropping point of greases determination

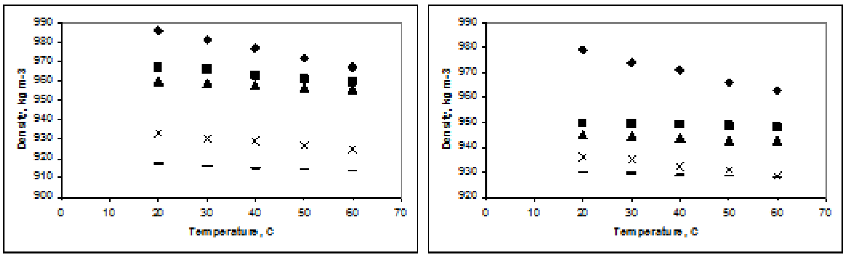
The dropping point of greases was measured according the Ubbelohde method standard DIN 51801-2 . The dropping point is a measure of the grease's consistency and allows the comparison of different formulations.

Results and discussion

Variation of greases density with temperature

Apart from the need of density value for the calculations of dynamic viscosity, the variation of density with temperature is an indicator of the dispersion quality.

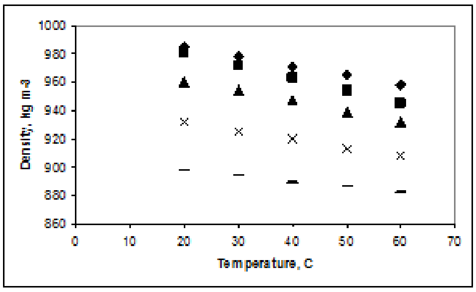
As seen in figure 1, every single grease shows a good linearity of the density with temperature, with correlation factors between r^2= 0.9708 and r^2=1. The slopes of the lines were smaller for greases proceeding from corn oil (between m=-0.041and m=-0.4), slightly higher for greases proceeding from olive oil (between m=-0.085and m=-0.47) and much higher for greases proceeding from palm oil (between m=-0.40 and m=-0.90). A higher slope is due to the higher density's variation with temperature of



a)

b)

Fig. 1. Variation of greases density with temperature
Legend: a -greases prepared with olive oil; b-greases prepared with corn oil; c- greases prepared with palm oil,
Legend - 10% soap; x 15% soap; Δ 20% soap; 25% soap; ♦ 30% soap



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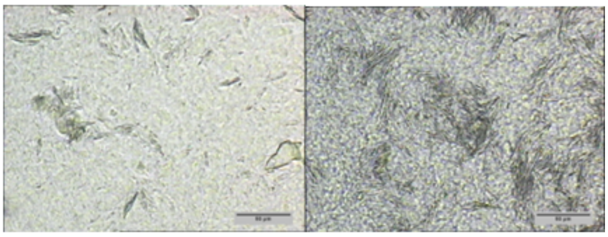


Fig. 2. Optical micrographs of representative greases samples: corn oil+ 15% wt soap and olive oil+15% wt soap, respectively - scale modulus 50μm

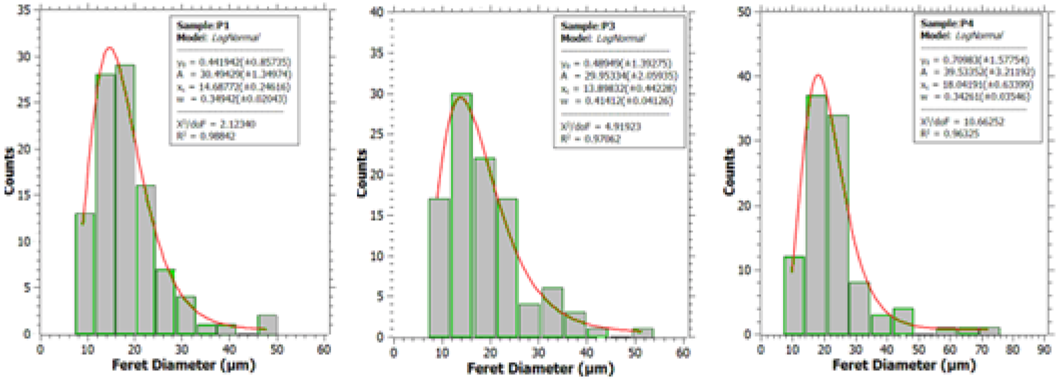
the base oil but can also indicate a poorer lubricating quality as it will be seen further when correlating with other characteristics.

Results of the morphological observations

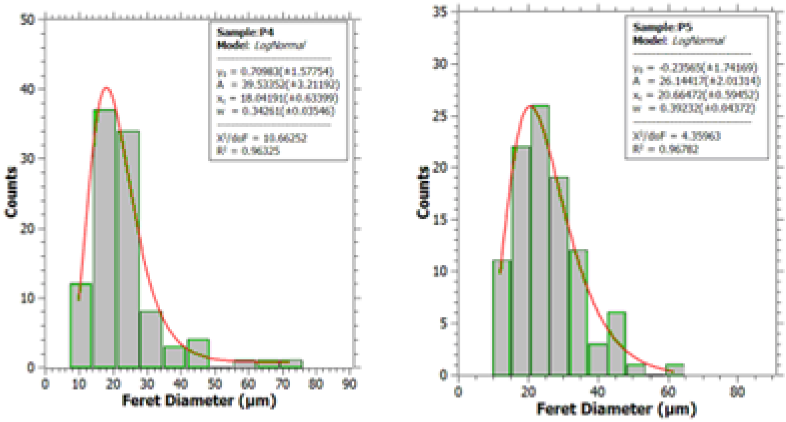
The optical micrographs revealed that the particulate form of the soap in the said preparation conditions consists in grains in a formed network, as seen in figure 2, for two representative samples. All the micrographs had the same aspect regardless of the soap concentrations.

The optical micrographs served for dimensions statistics. Soap grains have a medium size (Feret diameter) of 29 μm for the corn oil grease, 22 μm for olive oil grease and 15 μm for palm oil grease, depending inversely on the initial viscosity of the oil and independent of soap concentration. The size was measured for 50-100 grains in each micrograph and lognormal function was used to estimate the central values of size distribution. As an example, in figure 3, the histograms for lubricating greases manufactured from corn oil with different concentration of soap are shown.

As seen in figure 3, the central size of soap grains is 29 μm regardless the soap concentration. Also, in each histogram appear 2-8 grains out of 100 with size over 60μm contributing to the increased viscosity of the grease. Even though the medium size is approximately the same in one type of grease, the viscosity increasing with soap concentration is due to the increased density of grains.



a) b) c)



d) e)

Fig. 3. Histogram of fiber/particle dimensions and lognormal function for lubricating greases with palm oil base stock (Counts vs.Feret diameter).
Legend: soap concentration in sample: a- 10%, b-15%, c-20%, d-25%, e-30%

Calculated skewness with values between +1 and +2 and kurtosis around +3 for all sample shows a distribution close to the normal, this indicating an uniform thermal treatment during the preparation of the greases.

Rheological study

The viscometer reports show the variation of shear stress (Pa) with shear rate (s^{-1}). The rheological curves indicate a thixotropic behaviour, as normal for any grease. In figure 4, the curves for the grease based on corn oil with 20% calcium stearate are shown at 20, 30, 40, 50 and 60 °C, but all the greases in this study had the same behaviour. The thixotropy is more emphasized for more concentrated dispersions (20-30% wt soap) and curiously, it is higher at 20 and 30°C, then decreases at 40 °C and 50°C and again increases at 60°C. This could be explained by the change in the dispersion system caused by rising temperature over a certain temperature, in this case over 50°C. At lower concentration of the soap (10 and 15% wt respectively), the thixotropy is not so obvious and tends to decrease continuously with rising temperature; in this case, the weak consistency allows the grease to behave similarly to the base oil.

By processing the rheological data, it resulted that the curves can be described by the power function (eq.1):

$$\tau = A \cdot \dot{\gamma}^{B} \qquad (1)$$

where τ is the shear stress, $\dot{\gamma}$ is the shear rate and A, B are constant.

The model described with eq.1 has positive constants A and B. Always: $0<B<1$. The rheological curves are accurately described by the power function since the correlation factors are between 0.9604 and 0.9974, as seen in tables 1-3. Worse correlation factors are noticed for some greases proceeding from corn oil and olive oil containing 30% wt soap (table 1 and table 2), which are almost solid at room temperature. The oil from the grease with 10% wt soap proceeding from palm oil separated after a week, so it wasn't analyzed from the rheological point of view, as seen in table 3.

The viscosity of fluids with a rheological behaviour described with the power law is then calculated with eq.2:

$$\eta = A \cdot \dot{\gamma}^{B-1} \qquad (2)$$

where η is the dynamic viscosity and $\dot{\gamma}$, A and B are the same as in eq.1, and their particular values for all the greases at different temperature are found in tables 1-3.

The values of A and B in tables 1-3 were calculated by the least squares method.

The graphical representation of the rheological curves as dynamic viscosity vs. shear rate is made in figures 5-7, for the greases with 20, 25 and 30% wt soap, those proved to be more consistent and with a better stability.

As one can see from figures 5-7, the viscosity at low shear rate (γ=9.97 s^{-1}) increases with the concentration of the soap. For example, in case of the grease based on corn oil, the values at 20 °C are: 0.35 Pa·s for 20%wt soap, 2.15 Pa·s for 25% wt and 3.99 Pa·s for 30%wt soap.

The power law governs the rheological curves. In general, the increasing temperature effect consists in decreasing viscosity. An irregularity is noticed: when the temperature increases over 50°C, most of the greases becoming more viscous at low shear rate. This demonstrates a change in the oil-soap dispersion system properties. However, at high shear rate the rule is always the same: the viscosity decreases with increasing temperature. Also, comparing figure 3 and figure 4 on one side with figure 5 on the other side, one can conclude that greases prepared with palm oil are more sensitive to temperature since the viscosity varies more with temperature than in the case of the greases based on olive oil and corn oil.

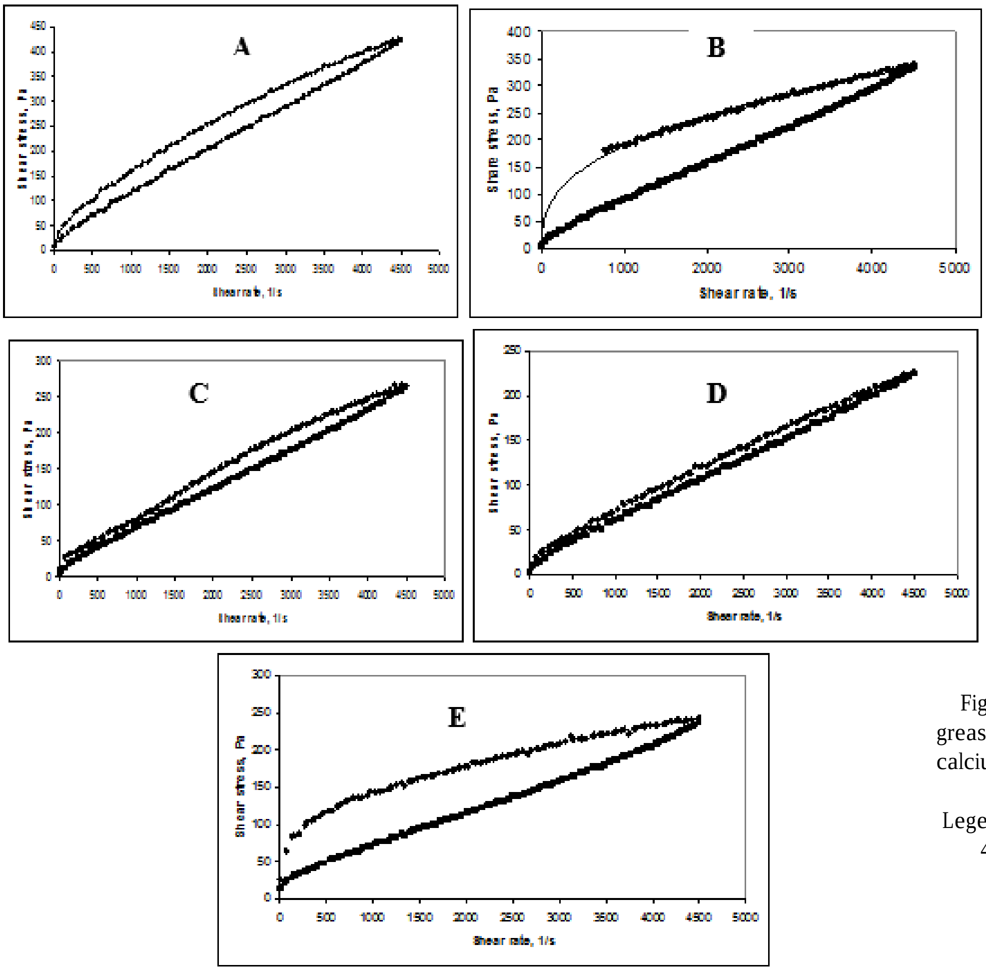


Fig. 4. Rheological curves of the grease based on corn oil with 20% wt calcium stearate (Shear stress, τ [Pa] vs. Shear rate, $\dot{\gamma}$ [s^{-1}])
Legend: A- at 20 °C; B- at 30 °C; C- at 40 °C; D- at 50 °C; E- at 60 °C.

Table 1
POWER LAW CORRELATIONS FOR THE RHEOLOGICAL CURVES OF GREASES BASED ON OLIVE OIL AND CALCIUM STEARATE

Soap concentration	Temperature	Coefficients of rheological equation (Eq.1) for increasing shear rate	Correlation coefficient for increasing shear rate, r^2	Coefficients of rheological equation (Eq.1) for decreasing shear rate	Correlation coefficient for decreasing shear rate, r^2
10% wt	20 °C	A=20.30 B=0.30	0.978	A=1.65 B=0.69	0.984
	30 °C	A=10.81 B=0.42	0.9842	A=0.65 B=0.74	0.9943
	40 °C	A=0.63 B=0.63	0.9753	A=0.28 B=0.74	0.9954
	50 °C	A=0.50 B=0.71	0.9810	A=0.84 B=0.50	0.9618
	60 °C	A=1.78 B=0.57	0.9604	A=1.24 B=0.63	0.9841
15% wt	20 °C	A=8.74 B=0.52	0.9909	A=0.82 B=0.69	0.9940
	30 °C	A=1.22 B=0.69	0.9877	A=1.01 B=0.71	0.9810
	40 °C	A=0.82 B=0.69	0.9945	A=0.75 B=0.69	0.9805
	50 °C	A=0.75 B=0.67	0.9914	A=0.68 B=0.68	0.9863
	60 °C	A=0.93 B=0.64	0.981	A=1.01 B=0.63	0.9887
20% wt	20 °C	A=10.82 B=0.50	0.9819	A=8.37 B=0.52	0.9758
	30 °C	A=9.66 B=0.49	0.9973	A=5.88 B=0.53	0.9953
	40 °C	A=4.10 B=0.53	0.9819	A=2.90 B=0.57	0.9973
	50 °C	A=6.43 B=0.47	0.9758	A=3.87 B=0.53	0.9811
	60 °C	A=27.34 B=0.32	0.9970	A=6.26 B=0.48	0.9616
25% wt	20 °C	A=3.17 B=0.65	0.9995	A=2.65 B=0.66	0.9933
	30 °C	A=3.46 B=0.59	0.9818	A=2.48 B=0.63	0.9865
	40 °C	A=3.70 B=0.53	0.9873	A=1.80 B=0.62	0.9921
	50 °C	A=1.37 B=0.63	0.9926	A=3.31 B=0.51	0.9716
	60 °C	A=6.63 B=0.43	0.9888	A=1.30 B=0.63	0.9973
30% wt	20 °C	A=16.88 B=0.35	0.8417	A=1.24 B=0.72	0.9453
	30 °C	A=6.56 B=0.39	0.9780	A=0.0098 B=0.93	0.9159
	40 °C	A=29.50 B=0.36	0.9515	A=0.36 B=0.77	0.9927
	50 °C	A=2.81 B=0.31	0.9970	A=0.21 B=0.84	0.9966
	60 °C	A=22.84 B=0.31	0.9284	A=0.52 B=0.73	0.9857

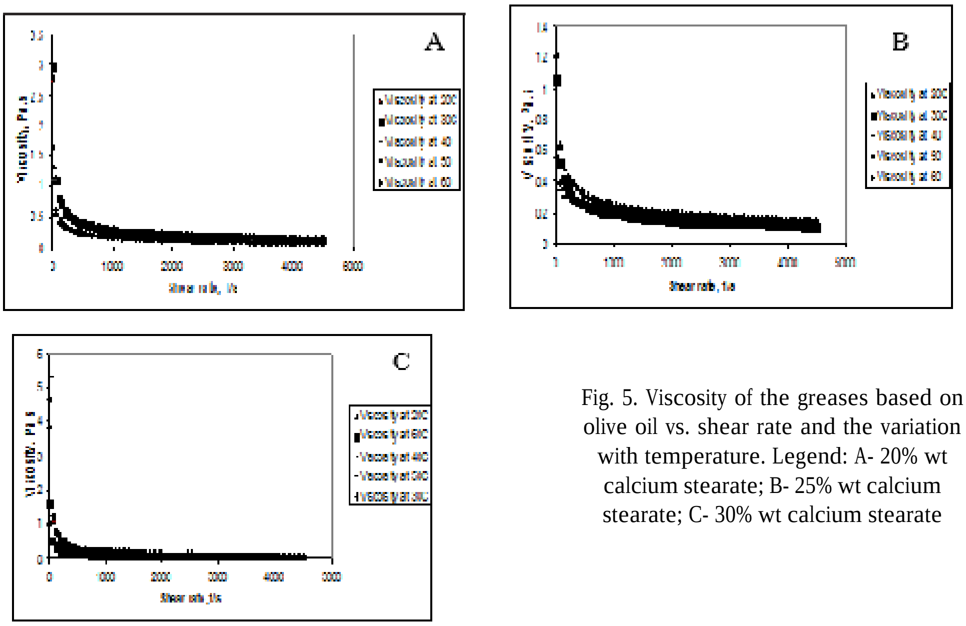


Fig. 5. Viscosity of the greases based on olive oil vs. shear rate and the variation with temperature. Legend: A- 20% wt calcium stearate; B- 25% wt calcium stearate; C- 30% wt calcium stearate

Table 2
POWER LAW CORRELATIONS FOR THE RHEOLOGICAL CURVES OF GREASES BASED ON CORN OIL AND CALCIUM STEARATE

Soap concentration	Temperature	Coefficients of rheological equation (Eq.1) for increasing shear rate	Correlation coefficient for increasing shear rate, r^2	Coefficients of rheological equation (Eq.1) for decreasing shear rate	Correlation coefficient for decreasing shear rate, r^2
10% wt	20 °C	A=66.75 B=0.27	0.9515	A=1.61 B=0.70	0.9920
	30 °C	A=2.15 B=0.61	0.9874	A=2.12 B=0.61	0.9775
	40 °C	A=2.15 B=0.58	0.9787	A=1.61 B=0.61	0.9870
	50 °C	A=2.01 B=0.57	0.9820	A=1.94 B=0.57	0.9783
	60 °C	A=2.34 B=0.55	0.9737	A=4.20 B=0.48	0.9820
15% wt	20 °C	A=1.69 B=0.67	0.9852	A=1.13 B=0.71	0.9751
	30 °C	A=3.55 B=0.57	0.9911	A=0.81 B=0.73	0.9954
	40 °C	A=0.29 B=0.78	0.9932	A=0.22 B=0.83	0.9979
	50 °C	A=0.46 B=0.73	0.9881	A=0.29 B=0.79	0.9967
	60 °C	A=11.52 B=0.38	0.9881	A=1.04 B=0.63	0.9770
20% wt	20 °C	A=2.35 B=0.62	0.9971	A=0.80 B=0.73	0.9874
	30 °C	A=14.16 B=0.38	0.9908	A=0.65 B=0.73	0.9867
	40 °C	A=1.33 B=0.62	0.9558	A=0.50 B=0.73	0.9810
	50 °C	A=0.89 B=0.65	0.9867	A=0.42 B=0.73	0.9881
	60 °C	A=14.55 B=0.33	0.9903	A=1.70 B=0.56	0.9503
25% wt	20 °C	A=7.36 B=0.46	0.9932	A=0.36 B=0.78	0.9709
	30 °C	A=39.11 B=0.28	0.9671	A=2.03 B=0.60	0.9945
	40 °C	A=17.84 B=0.34	0.9583	A=2.02 B=0.59	0.9938
	50 °C	A=6.47 B=0.44	0.9648	A=1.83 B=0.59	0.9935
	60 °C	A=105.6 B=0.14	0.9916	A=5.26 B=0.47	0.9979
30% wt	20 °C	A=84.30 B=0.39	0.9940	A=92.86 B=0.08	0.7820
	30 °C	A=72.98 B=0.26	0.8750	A=4.99 B=0.55	0.9671
	40 °C	A=14.49 B=0.39	0.9876	A=6.36 B=0.48	0.9602
	50 °C	A=23.82 B=0.32	0.9631	A=10.05 B=0.41	0.9673
	60 °C	A=45.64 B=0.22	0.9690	A=5.06 B=0.46	0.9577

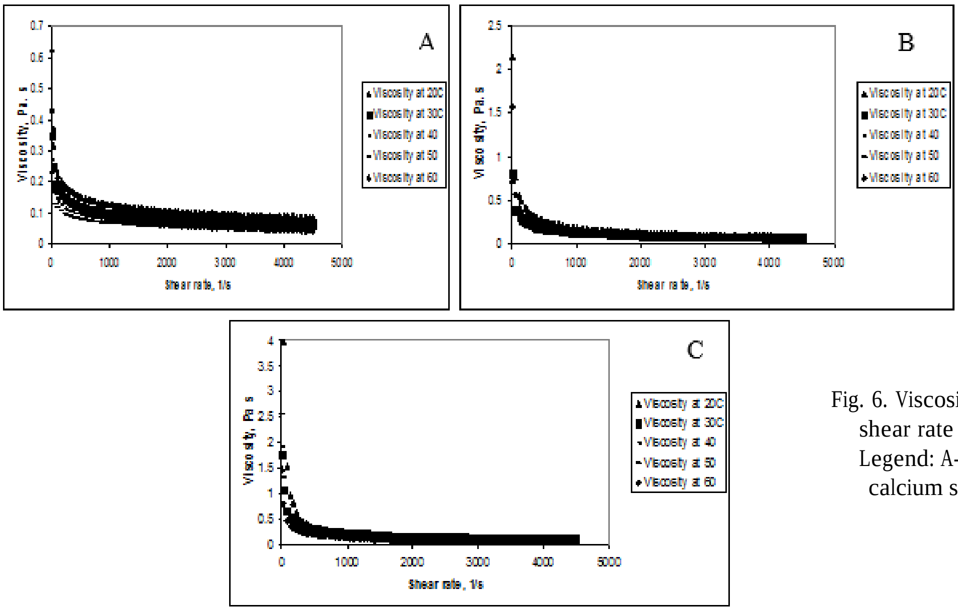


Fig. 6. Viscosity of the greases based on corn oil vs. shear rate and the variation with temperature. Legend: A- 20% wt calcium stearate; B- 25% wt calcium stearate; C- 30% wt calcium stearate

Table 3
POWER LAW CORRELATIONS FOR THE RHEOLOGICAL CURVES OF GREASES BASED ON PALM OIL AND CALCIUM STEARATE

Soap concentration	Temperature	Coefficients of rheological equation (Eq.1) for increasing shear rate	Correlation coefficient for increasing shear rate, r^2	Coefficients of rheological equation (Eq.1) for decreasing shear rate	Correlation coefficient for decreasing shear rate, r^2
15% wt	20 °C	A=4.02 B=0.56	0.9901	A=0.20 B=0.91	0.9987
	30 °C	A=0.29 B=0.81	0.9991	A=0.20 B=0.86	0.9956
	40 °C	A=0.26 B=0.80	0.9941	A=0.15 B=0.86	0.9946
	50 °C	A=0.49 B=0.71	0.9880	A=0.31 B=0.31	0.9837
	60 °C	A=2.52 B=0.51	0.9991	A=0.39 B=0.72	0.9865
20% wt	20 °C	A=10.79 B=0.49	0.9640	A=0.50 B=0.85	0.9965
	30 °C	A=0.45 B=0.81	0.9983	A=0.30 B=0.85	0.9954
	40 °C	A=0.36 B=0.76	0.9980	A=0.13 B=0.89	0.9990
	50 °C	A=1.39 B=0.57	0.9414	A=1.38 B=0.57	0.9468
	60 °C	A=0.20 B=0.79	0.9933	A=0.27 B=0.75	0.9795
25% wt	20 °C	A=71.63 B=0.29	0.9010	A=2.10 B=0.70	0.9907
	30 °C	A=1.75 B=0.97	0.9914	A=0.97 B=0.73	0.9909
	40 °C	A=1.43 B=0.62	0.9937	A=0.79 B=0.69	0.9884
	50 °C	A=1.07 B=0.63	0.9885	A=0.83 B=0.70	0.9981
	60 °C	A=0.84 B=0.64	0.9873	A=0.61 B=0.69	0.9971
30% wt	20 °C	A=3.35 B=0.61	0.9984	A=1.24 B=0.72	0.9949
	30 °C	A=9.95 B=0.45	0.9845	A=0.70 B=0.76	0.9971
	40 °C	A=0.66 B=0.72	0.9828	A=0.27 B=0.83	0.9981
	50 °C	A=1.15 B=0.64	0.9855	A=0.58 B=0.72	0.9879
	60 °C	A=30.47 B=0.28	0.9940	A=1.45 B=0.62	0.9916

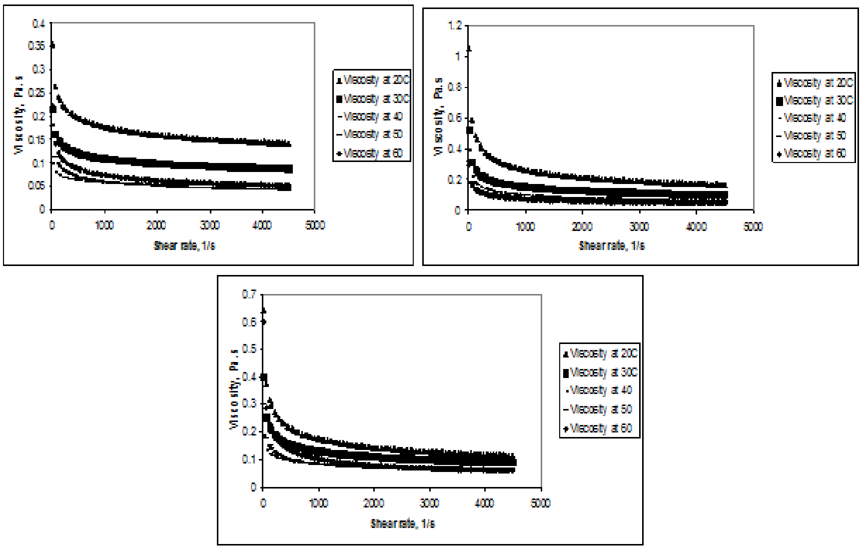


Fig. 7. Viscosity of the greases based on palm oil vs. shear rate and the variation with temperature. Legend: A- 20% wt calcium stearate; B- 25% wt calcium stearate; C- 30% wt calcium stearate

Table 4
VISCOSITY OF SOME VEGETABLE OIL BASED GREASES COMPARATIVELY WITH PARAFFINIC OIL BASED GREASE WITH 20% WT CALCIUM STEARATE (STERPU ET AL, 2011), AT $\dot{\gamma}$=9.97 s^{-1}

Temperature	Grease with mineral oil and 20% wt calcium stearate	Grease with olive oil and 25% wt calcium stearate	Grease with corn oil and 25% wt calcium stearate
20 °C	2.51 Pa·s	2.40 Pa·s	2.15 Pa·s
30 °C	1.57 Pa·s	1.35 Pa·s	1.20 Pa·s
40 °C	0.78 Pa·s	1.26 Pa·s	0.79 Pa·s

By comparing the viscosity of the greases prepared from vegetable oils with those obtained through the same preparation method from paraffinic mineral oil with 20% wt calcium stearate, it was found that some greases prepared from corn oil and olive oil with 25% wt soap, are very similar, as seen in table 4.

Greases obtained from olive oil with 20 and 25% wt soap and all greases with 30% wt soap have higher viscosity in the same conditions.

Table 5
DROPPING POINTS OF GREASES BASED ON VEGETABLE OIL AND CALCIUM STEARATE

Concentration of the soap, % wt	Dropping point, °C		
	Olive oil based greases	Corn oil based greases	Palm oil based greases
10	-	-	-
15	46	90	-
20	56	98	75
25	67	102	84
30	86	107	94

Dropping points of the greases

The dropping point is related to the consistency of the grease and serves to estimate the maximum temperature for working conditions. The benchmark grease prepared from paraffinic mineral oil with 20% wt calcium stearate has a dropping point of 91°C (determined in standard conditions according to DIN 51801-2) so that the grease is characterized as soft. The dropping points of greases prepared from vegetable oil are shown in table 5.

Dropping points could not be determined in case of all greases with 10 %wt soap neither for the grease based on palm oil with 15% wt were the oil was partially separated after a few weeks from preparation, when the measurements took place. Comparing with the benchmark grease, the corn oil greases were superior to that one in all concentrations of soap, the palm oil greases with 25-30% were comparable and olive oil greases were inferior.

The dropping points of the greases can characterize the greases as *soft* and this is due both to the base oil low viscosity and to calcium soap, so they couldn't be used at higher temperature, but some of them can be considered for applications in milder conditions such as chassis greases or sealing grease for food equipment also taking into account their lack of toxicity.

Conclusions

The rheological study of greases prepared from olive oil, corn oil and palm oil with calcium stearate in concentrations from 10 to 30% wt, together with their morphological and melting characterization leads to the following conclusions:

- due to their consistency, rheological behaviour, stability, non-toxicity and waterproof properties, the greases with concentrations of 20-25% wt calcium stearate obtained from the said vegetable oils can be characterized as *soft* and used for lubrication purposes in milder conditions such as sealing greases for food equipment or for chassis lubrication;

-greases with 10-15% wt soap are not recommended for these purposes due to their feeble stability and those with 30% wt soap (except those obtained from olive oil) are too consistent at the environmental temperature so their application on the surfaces is difficult;

-the greases obtained from olive oil have lower dropping points this is why their use should be restricted to temperature below 50°C even for higher concentrations of soap;

-additivation could improve the properties of the studied greases so the next step in developing commercial greases should be an extensive study of greases including supplementary additives.

Improvements in the stability and rheological behaviour of these greases should be studied in the future with additivation of some natural polymers, in order to preserve the non- toxicity of the grease and without affecting the waterproof properties of the greases.

References

1.MAS, R., MAGNIN, A., J. Rheol., vol. 38, 1004, p.889
2.NATIONAL LUBRICATING GREASE INSTITUTE , Lubricating Greases Guide, Kansas City, 2006
3.RUDNICK,L.R., Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology. CRC Press, Taylor & Francis Group, Boca Raton, Florida, 2006
4.TEODORESCU, N., Proceedings Scientific International Conference, Inter-Ing, Tg. Mureº, vol. I, 2003, p.205
5.MANG, T., DRESEL, W., Lubricants and Lubrication, Second Edition, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2007
6.TEODORESCU, N., Rev. Chim.(Bucharest), **56**, no. , 2005, p.27
7.TEODORESCU, N., PRODEA, I-M., STEFANESCU, M-F., Journal of Engineering Studies and Research, vol. 19, 2013, p.65
8.CANN, P.M., SPIKES, H.A., STLE Tribol. Trans., vol. 48, 1992, p.335
9.CANN, P.M., DONER, J.P., WEBSTER, M.N., WICKSTROM, V., STLE Tribol. Trans., vol. 44, 2001, p. 399
10.COURONNE, I., BLETTNER, G., VERGNE, P., STLE Tribol. Trans., vol. 43, 2000, p. 619 11.COURONNE, I., VERGNE, P., STLE Tribol. Trans., vol. 43, ,2000, p.788
12.KAGEYAMA, H., MACHIDORI, W., MORIUCHI, T., NLGI Spokesman, vol.53, 1984, p.246
13.BARTZ, W.J.,Tribol. Int., vol.31, 1998, p. 35
14] BOGATU, L., CIUPARU, D., TÃNÃSESCU, C., Rev.Chim.(Bucharest), **61**, no.10, 2010, p.1003
15.BOGATU, L., DRAGOMIR, R., Rev.Chim.(Bucharest), **66**, no.5, 2015, p.722
16.BOGATU, L., TANASESCU, C., Jurnal of the Balkan Tribological Association, vol. 12 (4), 2006, p 566
17.ANANDAN, N., JAGGA, C.R., PANDLEY, R.K., STLE Tribol. Trans., vol 2, 2007, p. 34
18.HURLEY,,S., CANN, P.M., NLGI Spokesman, vol. 63, 1999, p. 12
19.KIMURA, H., IMAI, Y., YAMAMOTO, Y., STLE Tribol. Trans., vol. 44, 2001, p. 405
20.NAKA, M., ITO, H., KOIZUMI, H., SUGIMORI, Y., STLE Tribol. Trans., vol. 41, 1998, p.387
21.SANCHEZ, R., FRANCO, J.M., DELGADO, M.A., VALENCIA, C., GALLEGOS, C.. Carbohydr. Polym., vol. 83, 2011, p. 151
22.MARTIN-ALFONSO, J.E., NUNEZ, N., VALENCIA, C., FRANCO, J.M., DIAZ, M.J., J., Ind. Eng. Chem., vol.17, 2011, p. 818
23.FRANCO, J.M., DELGADO, M.A., VALENCIA, C., SANCHEZ, M.C., GALLEGOS, C. , Chem. Eng. Sci. 60, 2005, p.2409
24.NUNEZ, N., MARTIN-ALFONSO, J.E., VALENCIA, C., SANCHEZ, M.C., FRANCO, J.M., Ind. Crops Prod, 2012, vol. 37, p. 500
25.GARCIA-ZAPATEIRO, L.A., VALENCIA, C, FRANCO, J.M..Ind. Crops Prod., 2014, vol. 54, p.115
26.STERPU, A.E., TEODORESCU, N., PRODEA, I.M., NEAGU, A.A., DUMITRU, A.I., Int. Rev. Chem. Eng. Rapid Communications., 2010, vol. 2, p.81.
27.STERPU, A.E., TEODORESCU, N., PRODEA, I.M., POPESCU, E., NITA I., Environ. Eng. Manag. J., vol.9, 2010, p.1063
28.WILSON, B., Ind. Lubr. Tribol. 50, 1998, p.6
29.RAJEWSKI, T.E., FOKENS, J.S., WATSON, M.C., Ind. Lubr. Tribol, vol. 52, 2000, p.110 30.ADHVARYU, A., SUNG, C., ERHAN, S.Z., vol. 21, 2005, p.285
31.DRESEL, W.H., Ind. Crops Prod., vol.2, 1994, p.281
32.ADHVARYU, A., ERHAN, S.Z., PEREZ, J.M., Wear, vol. 257, 2004, p.359
33.DICKEN, T.W., Ind. Lubr. Tribol., vol. 46, 1994, p.3
34.ERHAN, S.Z., SHARMA, B.K., PEREZ, J.M., Ind. Crops Prod., vol. 24, 2006, p.292.

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