Eco-friendly Additivated Lubricating Greases Made of Agricultural Resources

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The purpose of this work is to to develop a simple technology for producing high quality greases from renewable and handy resources in a specific region: West Africa. New lubricating greases were formulated based on palm oil and corn oil with 20% wt. calcium stearate prepared in situ at 100ºC and by adding during manufacture crystalline cellulose or Kraft lignin in different concentration (5%, 10% or 20% w/w). These additives significantly improve the rheological parameters, consistency and mechanical stability of the products. Products with 20% (w/w) cellulose or 20% (w/w) lignin added are of particularly good quality These greases could be used in domestic economy, for the agricultural equipment, but also in other industries such as food industry or paper mills being suitable for valves and fittings, gearboxes, rolling bearing.

Keywords: green manufacturing; agricultural resource; lubricating eco-friendly grease.

Vegetable oils can be used as they are to replace mineral lubricant oils, or in lubricant greases formulae, because their rheological properties are very close to those of mineral oils. Also, they are affordable, more eco-friendly and with lower toxicity [1]. On the other hand, vegetable oils products also present certain disadvantages, for instance poor oxidative stability [2], poor thermal stability [3], or mechanical bad performance [4,5].

In order to improve the lubricating greases performances, it is desirable to incorporate additives during the greases manufacture process. These additives modify the interfacial energy between the base oil and the thickener agent particles, and their effectiveness depends mainly on their nature, as well as on their volumetric fraction in product [6,7]. Polymers are often used as additives, in order to upgrade some special properties like consistency, dropping point or water resistance [8], to promote the adhesion and cohesion and also to improve mechanical and chemical stability at high and low temperatures [7,9]. When using a polymer additive, the rheological properties of greases change because it acts as a thickening agent. Used as supplements to the traditional thickening agents, polymers also decrease the soap content by keeping constant the consistency or even can increase the consistency of greases for some specific applications. The rheological modifications induced by polymeric additives affect the viscoelasticity of lubricating greases, thus improving sealing and flow properties under working conditions [10].

Typical grease contains 75–95% base oil, 5–20% thickener (soap) and 0–20% additives [11].

Two of the most important polymers obtained from renewable resources, cellulose pulp and lignin may represent an interesting alternative to replace synthetic additives. Moreover, these polymers are available in large quantities, exhibit excellent processability, a wide range of good characteristics, at lower costs.

Cellulosic derivatives are biodegradable, that can provide suitable rheological properties to lubricating greases formulations [12,13]. On the other hand, lignin, a cross-linked polymer type, is a by-product of paper and timber industry, which consists of sulfonate, phenylic hydroxyl, alcoholic hydroxyl and hydrophobic groups included in the carbon chain [14,15].

In this work, we intent to evaluate the effect that cellulose and lignin additives on mechanical and rheological properties of traditionally calcium lubricating greases based on palm oil and corn oil.

The final goal of the study is to develop a simple technology for producing high quality greases from renewable and handy resources in a specific region (West Africa after origin of first author). These greases could be used in domestic economy, for the agricultural equipment, but also in other industries such as food industry or paper mills.

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Experimental part

Materials

Two vegetable oils were selected for the manufacture of lubricant greases: unrefined corn oil (32.108 cSt at 40°C, 905 kg/m^3 at 40°C) and palm oil (35.41 cSt at 40°C, 880 kg/m^3 at 40°C).

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 vegetable oil.

Natural polymers like crystalline cellulose and Kraft lignin provided by Merck were used as additives.

Manufacture of the lubricant greases

The anufacturing process was described by Sterpu et al, 2016 [1]. The base grease was prepared by producing the soap thickener *in situ*. The vegetable oil, stearic acid and $Ca(OH)_2$ were mixed from the beggining, heated up to 100 °C and maintained under agitation for one hour, to complete the saponification reaction. The proportion of raw materials in the formula was calculated to have in the end the desired soap concentration (20% wt) , in batches of 500 g: 400g oil +93.7 g stearic acid+12.2 g $Ca(OH)_2$. The 5.9 g surplus represents the water formed in saponification reaction which is partially removed by vaporisation during the synthesis. Eight batches were produced in parallel. Cellulose or lignin were added during synthesis, towards the end of the process, under mixing. Then the product was set to cool by natural convection.

Characterisation of greases

Density determination

Greases density determination was carried out according to NYE CTM003 cup method for density and specific gravity of lubricating greases, which originally is made at 25°C . In this case, the standard method was adapted for density determinations at higher temperature: 20 °C, 30°C, 40°C, 50°C. These measurements are necessary for dynamic viscosity calculations.

Rheological measurements

A plate-cone rheoscope Haake VT 550, was used for rheological measurements. The construction of the apparatus allows shear rates in range of 9.97 – 4500 s^{-1}, corresponding to 2 - 964 rotations per minute.

The samples were characterized at temperature of 20, 30, 40 and 50°C, with increasing and decreasing shear rate.

The rheological reports provided by the software contain the variation of shear stress vs. shear rate, in 100 points.

Penetration tests

The penetration indexes of greases samples were determined, before and after the mechanical stability test, by using a Richardson Cone Standard Penetrometer, Romanian standard STAS 42 – 68. According to the method, the consistency of grease is measured by dropping a cone of known mass into the grease sample and recording the penetration depth. A low value of penetration means firm grease with good consistency The penetration values of the samples are converted to NLGI grades [16]. The National Lubricating Grease institute classifies the consistency of greases from to 6 grade.

Dropping point of greases

Lubricating greases dropping point is another measure of its consistency and it allows the comparison between different formulations. In this work, dropping point of greases was measured according the Ubbelohde method standard DIN 51801-2.

Mechanical stability tests

500 mL samples of additivated greases were "worked" by shear mixing, in an agitator for 50 minutes at 200 rot/min (equivalent of 10 000 strokes). In greases terminology, grease before the test is named „unworked” and after the test is „worked”.

The mechanical stability of all greases was evaluated as the difference between penetration values before and after shear mixing. These differences indicate the mechanical stability of the grease.

Results and discussions

Taking into account the rheology and consistency of base greases (Vodounon ș.a., 2019) [19], two of them were selected for additivation: palm oil and corn oil based containing 20% wt. soap, manufactured at 100 °C. Even though greases with 25% wt. soap showed the highest apparent vicosity and consistency, they were too stiff at 20 °C.

Greases with 15% wt. were too soft. Greases with 20% wt. behave well and are also onctuous, but their consistency and viscosity are prone to improvment through additivation. By adding cellulose (10% or 20% w/w) or lignin (5% or 20% w/w) to both vegetable oils, 8 products resulted.

Density of additivated greases

The additivated greases showed higher density values than the base greases. The increase was bigger when adding cellulose (by 38 kg $m^{-3}$for corn oil grease with 20% w/w cellulose and 66 kg $m^{-3}$for palm oil grease with 20% w/w cellulose) compared with adding lignin (by 18 kg m^{-3} for corn oil grease with 20% w/w lignin and 46 kg $m^{-3}$for corn oil grease with 20% w/w lignin).

The slope density vs. temperature line decreased significantly from -2.03 kg m^{-3}°C^{-1} for corn oil base grease to – 0.80 when adding 20% (w/w) cellulose and -0.93 kg m^{-3}°C^{-1} when adding 20% (w/w) lignin. This indicates an improvement in the dispersion grade.

Additivated palm oil greases had slopes around the base grease (-0.38 kg m^{-3}°C^{-1} when adding 20% w/w cellulose and -0.83 kg m^{-3}°C^{-1} when adding 20% w/w lignin, comparing with -0.65 kg m^{-3}°C^{-1} for the base grease).

Additivated greases rheology

These greases where characterized immediately after the manufacture and then after a working test by shear mixing described in section 2.3.5.

The additivated greases are Bingham fluids obeing the Bingham law (eq.1) where: τ_0 is the threshold (Pa), μ_p- the plastic viscosity (kg m^{-1} s^{-1} or N s m^{-2}) and $\dot{\gamma}$ is the shear rate (s^{-1}). The apparent viscosity (μ_a) at a certain value of shear stress, can be calculated with Eq.2.

$$\tau = \tau_0 + \mu_p \cdot \dot{\gamma} \quad (1)$$

$$\mu_a = \mu_p + \frac{\tau_0}{\dot{\gamma}} \quad (2)$$

In Table 1, a comparison between the base greases [17] and the additivated ones, immediately after manufacture is shown in Table 1 from the viewpoint of the apparent viscosity at 20°C at $\dot{\gamma}$ =4500 s^{-1}.

Table 1

APPARENT VISCOSITY AT $\dot{\gamma}$ = 4500 s^{-1} AND 20°C OF ADDITIVATED GREASES MANUFACTURED AT 100°C WITH 20% CALCIUM STEARATE

Base oil	$\mu_a(Pa \cdot s)$ for grease before additivation	$\mu_a(Pa \cdot s)$ for grease with 10% cellulose	$\mu_a(Pa \cdot s)$ for grease with 20% cellulose	$\mu_a(Pa \cdot s)$ for grease with 5% lignin	$\mu_a(Pa \cdot s)$ for grease with 20% lignin
Corn oil	0.1901	0.2149	0.4346	0.1576	0.5007
Palm oil	0.1876	0.3003	0.4837	0.2192	0.4742

Comparing with the base greases , by adding cellulose or lignin to grease results in obvious increase of the viscosity. For example, comparing them at 20°C, the viscosity of the corn oil based grease increases by 13 % when adding 10% (w/w) cellulose and by 128 % when adding 20% (w/w) cellulose. By adding 20% (w/w) lignin, the viscosity increases by 163%. The corn based grease with added 5% (w/w) lignin was structurally unstable, with oil separating after 7 days, this is why the apparent viscosity was lower, and further the working test couldn't be performed.

The increase of apparent viscosity for palm oil based greases was by 60% when adding 10% (w/w) cellulose and by 158 % when adding 20% (w/w) cellulose. By adding 5% (w/w) lignin, its viscosity increased by 16.8% and with 20% (w/w) lignin it increased by 153%.

The complete sets of rheological parameters of additivated greases together with the apparent viscosities μ_a at $\dot{\gamma}$ =4500 s^{-1} , immediately after manufacture ("unworked grease") and after the shear mixing test („worked grease"), are presented in Tables 2-5.

Table 2

THE PARAMETERS OF BINGHAM LAW MODEL FOR GREASES MADE OF CORN OIL AT 100 ^{O}C, WITH 20% wt. SOAP AND ADDING CELLULOSE, BEFORE AND AFTER THE SHEAR MIXING TEST

Cellulose concentration, %wt	Rheological test temperature, °C	Parameters of the unworked grease				Parameters of the worked grease				Relative difference between μ_a values before and after test %
		τ_0, Pa	μ_p, Pa·s	r^2	μ_a, Pa·s	τ_0, Pa	μ_p, Pa·s	r^2	μ_a, Pa·s	
10	20	64	0.2006	0.9973	0.2149	51	0.1485	0.9975	0.1598	25.64
	30	49	0.1134	0.9989	0.1243	37	0.0987	0.9899	0.1069	20.91
	40	44	0.0732	0.9983	0.0830	35	0.0534	0.9931	0.0612	34.06
	50	59	0.0519	0.9758	0.0650	39	0.0367	0.9762	0.0454	41.92
20	20	375	0.3512	0.9855	0.4346	249	0.2147	0.9933	0.2700	10.08
	30	125	0.2159	0.9957	0.2187	73	0.1431	0.9952	0.1593	28.11
	40	100	0.1500	0.9948	0.1722	53	0.0902	0.9957	0.1020	11.29
	50	82	0.1037	0.9948	0.1219	49	0.0703	0.996	0.0812	33.51

Table 3

THE PARAMETERS OF BINGHAM LAW MODEL FOR GREASES MADE OF CORN OIL AT 100 ^{O}C, WITH 20% wt. SOAP AND ADDING LIGNIN, BEFORE AND AFTER THE SHEAR MIXING TEST

Lignin concentration, %wt	Rheological test temperature, °C	Parameters of the unworked grease				Parameters of the worked grease				Relative difference between μ_a values before and after test %
		τ_0, Pa	μ_p, Pa·s	r^2	μ_a, Pa·s	τ_0, Pa	μ_p, Pa·s	r^2	μ_a, Pa·s	
5	20	57	0.1449	0.9968	0.1576	N/A	N/A	N/A	N/A	N/A
	30	52	0.1006	0.9959	0.1122	N/A	N/A	N/A	N/A	N/A
	40	53	0.0723	0.9954	0.0841	N/A	N/A	N/A	N/A	N/A
	50	44	0.0476	0.9935	0.0574	N/A	N/A	N/A	N/A	N/A
20	20	480	0.3940	0.9816	0.5007	92	0.3224	0.9975	0.3428	31.52
	30	395	0.3217	0.9870	0.4095	94	0.2340	0.9978	0.2549	37.75
	40	262	0.2532	0.9903	0.3114	89	0.1790	0.9952	0.1988	36.17
	50	168	0.1953	0.9930	0.2326	68	0.1814	0.9967	0.1965	15.53

Table 4

THE PARAMETERS OF BINGHAM LAW MODEL FOR GREASES MADE OF PALM OIL AT 100 ºC, WITH 20% wt. SOAP AND ADDING CELLULOSE, BEFORE AND AFTER THE SHEAR MIXING TEST

Cellulose concentration, %wt	Rheological test temperature, °C	Parameters of the unworked grease				Parameters of the worked grease				Relative difference between μ_a values before and after test %
		τ_0, Pa	μ_p, Pa·s	r^2	μ_a, Pa·s	τ_0, Pa	μ_p, Pa·s	r^2	μ_a, Pa·s	
10	20	158	0.2652	0.9918	0.3003	249	0.2147	0.9933	0.2700	10.08
	30	117	0.1823	0.9938	0.2083	73	0.1431	0.9952	0.1593	23.51
	40	133	0.0854	0.9783	0.1150	53	0.0902	0.9957	0.1020	11.29
	50	78	0.1050	0.9959	0.1223	49	0.0703	0.9960	0.0812	33.63
20	20	507	0.371	0.9857	0.4837	380	0.3865	0.9857	0.4709	2.63
	30	220	0.2607	0.9899	0.3096	207	0.2645	0.9900	0.3105	-0.29
	40	120	0.1717	0.9943	0.1984	86	0.1698	0.9973	0.1889	4.77
	50	64	0.1064	0.9945	0.1206	63	0.1148	0.9949	0.1288	-6.78

Table 5
THE PARAMETERS OF BINGHAM LAW MODEL FOR GREASES MADE OF PALM OIL AT 100 ^{O}C, WITH 20% wt. SOAP AND ADDING LIGNIN, BEFORE AND AFTER THE SHEAR MIXING TEST

Lignin concentration, %wt	Rheological test temperature, °C	Parameters of the unwoaddidivatedrked grease				Parameters of the worked grease				Relative difference between μ_a values before and after test %
		τ_0, Pa	μ_p, Pa·s	r^2	μ_a, Pa·s	τ_0, Pa	μ_p, Pa·s	r^2	μ_a, Pa·s	
5	20	94	0.1983	0.9968	0.2192	92	0.1891	0.9975	0.2095	4.40
	30	75	0.1358	0.9978	0.1525	94	0.1387	0.9978	0.1596	-4.67
	40	63	0.0930	0.9739	0.1070	89	0.1018	0.9952	0.1216	-13.62
	50	52	0.0537	0.9959	0.0653	68	0.0686	0.9967	0.0837	-28.28
20	20	297	0.4082	0.9946	0.4742	279	0.395	0.9940	0.4570	3.63
	30	435	0.2729	0.9753	0.3696	271	0.2789	0.9887	0.3391	8.24
	40	333	0.2173	0.9808	0.2913	229	0.2079	0.9903	0.2588	11.16
	50	245	0.1541	0.9819	0.2085	190	0.158	0.9893	0.2002	3.99

Following the wearing test, the viscosity decreased by 25.69% on the average for corn oil based greases additivated with cellulose, respectively by 30.42% when additivated with lignin. The palm oil based greases behaved better with only 19.63% decrease in viscosity when additivated with 10 % (w/w) cellulose and very close to the original viscosity for those additivated with lignin 5% (w/w) or 20% (w/w) cellulose or lignin.

From the point of view of rheology and mechanical stability, the best results were obtained with palm oil based greases additivated with 20% lignin.

Cone penetration and mechanical stability

After additivation, it can be noticed that greases samples penetration index decreases when the additive concentration increases, especially in the case of cellulose, this meaning an improvment in consistency.

Traditionally, mechanical stability of a lubricating grease is defined as the difference between penetration indexes after and before submitting the grease to a work test. Greases with good mechanical stability characteristics must present penetration increments close to zero after working.

Table 6 collects the penetration values of greases samples before and after submitting the samples to the shear mixing test, their differences (penetrations variations) , the corresponding NLGI grades of unworked samples, and those for worked samples.

Table 6
PENETRATION INDEXES OF GREASES MANUFACTURED AT 100^{O}C , UNWORKED AND WORKED

Grease sample	Penetration of the unworked sample [x 10^{-1} mm]	NLGI grade of the unworked sample	Penetration of the worked sample [x 10^{-1} mm]	Penetration variation [x 10^{-1} mm]	NLGI grade of the worked sample
Grease from palm oil with 20% wt soap +cellulose 10% (w/w)	176	4	235	59	3
Grease from palm oil with 20% wt soap +cellulose 20% (w/w)	102	6	160	58	5
Grease from palm oil with 20% wt soap +lignin 5% (w/w)	198	4	N/A	N/A	N/A
Grease from palm oil with 20% wt soap +lignin 20%(w/w)	175	4	180	5	4
Grease from corn oil with 20% wt soap +cellulose 10%(w/w)	144	5	304	160	5
Grease from corn oil with 20% wt soap +cellulose 20%(w/w)	109	6	241	132	5

Grease from corn oil with 20% wt soap +lignin 5%(w/w)	225	3	375	150	0
Grease from corn oil with 20% wt soap +lignin 20%(w/w)	105	6	204	99	4

The variation of penetration values is good for palm oil greases (below $60 \cdot 10^{-1}$ mm) and acceptable for greases from corn oil (100 – $160 \cdot 10^{-1}$ mm), since the worked greases are still hard (grade 4) or very hard (grade 5); the corn oil grease with 5% lignin wasn't tested because it was structurally unstable as discussed in section 3.2.2.

3.2.4. Greases dropping points

Dropping point is the temperature at which the grease passes from a semisolid to a liquid state under standard conditions. A low value of greases dropping point usually indicates that the matrix soap-vegetable oil is not firm. Dropping point is in relation with the grease consistency and must be in accordance with the temperature during equipment running.

Products drop points are presented in Table 7.

Table 7
DROPPING POINTS OF THE GREASES SAMPLES

Grease	Dropping Point, °C	
	unworked sample	worked sample
Grease from palm oil with 20% wt soap +cellulose 10% (w/w)	66	65
Grease from palm oil with 20% wt soap +cellulose 20% (w/w)	73	75
Grease from palm oil with 20% wt soap +lignin 5% (w/w)	74	72
Grease from palm oil with 20% wt soap +lignin 20%(w/w)	99	99
Grease from corn oil with 20% wt soap +cellulose 10%(w/w)	64	65
Grease from corn oil with 20% wt soap +cellulose 20%(w/w)	70	72
Grease from corn oil with 20% wt soap +lignin 5%(w/w)	53	53
Grease from corn oil with 20% wt soap +lignin 20%(w/w)	99	100

It was noticed that samples with added cellulose have lower dropping point than greases containing the same percent of lignin, so lignin gives firmer greases. Greases dropping point increases with additive concentration. Also, it can be observed that worked greases with 20% additive have a higher drop point than before the working test, indicating that mixing improve the dispersion of thickeners in the grease.

Conclusions

A study was conducted to find the optimum formulation of biodegradable greases made of sustainable resources. Greases were made up with vegetable oils, calcium stearate and vegetable additives.

Following a previous study concerning the influence of manufacture temperature and soap concentration on the rheological parameters and consistency [17], two base greases were selected: corn oil with 20% wt. calcium stearate and palm oil with 20% wt. calcium stearate, both manufactured at 100 ºC. The soap was synthesized during manufacturing and its characteristics were satisfactory, so that even though calcium based greases are usually classified as soft, these two formulations were promising.

The influence of cellulose and lignin concentration as additives on the rheological properties, consistency and mechanical stability has been investigated. Formulations with good rheological characteristics and mechanical stability were obtained by adding 20% (w/w) cellulose or lignin.

These products are suitable as gear grease but also in rolling bearings applications working at moderate temperature such as mechanisms for band conveyer in paper mills, food industry, agriculture. Also, they can be used in applications for incidental contact with materials in the food industry.

The manufacture is relatively simple and can be performed with agricultural resources, for the domestic market.

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