Additivation of vegetal oils for improving tribological characteristics

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Abstract. This paper presents a review on issues on additivating vegetal oils with friction and anti-wear modifiers. A SWOT analysis on vegetal oils reveals the shortcomings of these oils and the trend in their modification by the help of additives. Based on research reports available from literature and their experimental work, the authors formulated a synthesis on how the friction and wear modifiers act in lubricants and especially in vegetal oils. They discussed the influence of some friction and anti-wear modifiers added in vegetal oils, especially in soybean oil and rapeseed oil. The conclusion is that additivation of vegetal oils is still at the beginning as the reported results are not so efficient as compared to additivation of classical alternative - mineral oils and even less as compared to synthetic oils. But research must be continued as these vegetal oils become an actual resource for lubricant's base-stock.

1. SWOT analysis of vegetal oils as lubricants

The OECD presented a report on lubricants and additives in 2014 [1], [2] stating that vegetable oils have an upward trend in their use as lubricants, especially for areas with a stronger impact on the environment. Worldwide, 40 million tons of lubricants are consumed annually, while petroleum-based lubricants are still dominant. They begin to be challenged and replaced by synthetic oils and even by vegetal oils [3]. In 2016, Romania was the third largest producer of industrial seeds in the EU (rapeseed, soybean and sunflower).

Vegetal oils themselves may act as anti-wear additives and friction modifiers, due to strong interactions with the surfaces they come into contact with, especially metallic surfaces [4]. The long molecular chains of fatty acids and the presence of polar groups in the vegetal oil structure give them the ability to adhere and maintain on surfaces in contact, even under relatively severe regimes [5].

A SWOT analysis for introducing vegetal oils as lubricants showed that a set of properties should be considered when the designer decides this lubrication solution [6], [7].

Strengths include:
• biodegradability [8],
• environment protection or and acceptability (non-polluting or environmental friendly lubricants) [9], [10], [11],
• extraction from renewable resources (even with a reference to 100 years) or the possibility of recycling or re-use of the lubricant [3],
• high viscosity index [7],
• better flammability characteristics, auto ignition points and higher ignition temperature on hot surfaces [12], [13].
Weak points are especially related to the chemical composition of these oils as they consist of a mix of fatty acids (figure 1), the non-saturated having a great influence in weakening the reliability of oils as lubricants:

• lower viscosity as compared to mineral and synthetic oils [16], [17], [18], [19],
• oxidation [20], [12], [21] and poor chemical stability; there is a correlation between the unsaturation degree of a vegetal oil and its oxidative stability; the oxidation temperature and the oxidative stability can be predicted using each oil fatty acid composition rather than individual fatty acid percentage [22],
• sensitivity to moisture,
• operating temperature range lower than that of mineral and synthetic oils [23]; a bio-based lubricant will cause premature and possibly catastrophic equipment failure if the functioning temperature is over 105°C (and as low as 70...80°C for some vegetal oils); in extreme high-temperature, environmentally sensitive applications, biodegradable synthetic fluids are recommended,
• many of their properties are more time-dependent than those of mineral and synthetic oils,
• low temperature properties are poorer for vegetal oils than other lubricants [24],
• lower limit to seizure on four ball machine and sharp gradient to seizure limit (figure 2) [25].

Opportunities are supported by the following facts:

• complying with more stringent environmental protection requirements will minimize health and pollution risks,
• the high risk of exhaustion of petrol resources and the necessity of replacing them as an issue to be solved for the global economy.

The new market shares for organic and biodegradable lubricants (obtained from renewable resources, especially plants) have increased for areas such as hydraulic fluids, chain lubricants, mold lubricants, two-stroke engines, turbine fluids, etc. [9].

Environmentally acceptable lubricants are classified according to the type of base oil used in their formulation. In general, lubricants consist of approximately 75 to 90 % base oil [10].

![Figure 1. Diversity in fatty acid composition for vegetal oils. [14], [15]](image-url)
Figure 2. Evolution of WSD (wear scar diameter) with load to seizure limit for several vegetal oils [25].

Threats include:
- the need to re-design systems using bio-liquids, a solution that is possibly costlier,
- accepting lowering some system operating parameters (especially load and maintenance, but not limited to) [26],
- the still high price (but not forgetting that synthetic oils in the 1990s were almost 10 times more expensive than mineral ones and today the ratio is only 3 to 1), market and users inertia, the diversity of environmental and safety specifications and a global policy that has not yet been clearly addressed on environmental issues.

Literature reported relatively low or inconclusive results on nano lubricants [27], [28], [29], [30] mostly on transformer oil, gear oil and heat transfer oil. Limited investigations on the influence of nano additives on vegetal oils are presented [31], [32]. Even if modern equipment working under high load, speed and thermal conditions, require cooling and efficient lubrication, and for this concept, mineral and synthetic oils are still preferred, investigations on vegetal oils are needed for particular applications with environmental impact and in the perspective of oil resources extinction.

Chan et al. [33] propose criteria for the molecular structure of vegetal oils in order to have a good tribological behavior, based both on friction coefficient (stability, value and spread range) and wear measurements. The authors add several other parameters that would make the difference between poor and good quality of a lubricant: temperature in contact, durability (including oxidation), rates of different modifications, produced in time on the bodies involved in the tribosystem (solids and lubricant, environment). The bio-based oils include vegetable oils (VO), epoxidized VO, ring-opened products from epoxidized VO, estolides, and polyol esters. And the issue of additivating these oils is presented with recent advances: plant-derived compounds and polymers, particulate and layered materials, and ionic liquids.

Bio-based lubricants have also gained importance as alternatives to conventional petroleum-based lubricants in various applications, especially the automotive industry and green industries (food, wood, transport etc.). But these lubricants are still far from being practical substitutes. However, these shortcomings can be addressed by modifying the vegetable oils chemically or incorporating additives into these oils [31]. This review provides an overview of lubricants using vegetal oils as base and additives for improving their tribological behavior and useful information from authors’ experimental work for supporting the introduction of such lubricants in actual applications.
2. Nano additives for lubricants
Nanofluids containing solid nanoparticles could have a higher viscosity than common working fluids. But the actual effects of volume fraction, temperature, particle size, and shape on the viscosity of nano fluids are determined through experiments [34].

Early formulated vegetal oils used performance additives similar to those for petroleum oils that are, mostly, nonpolar, whereas triglycerides are highly polar. Thus, conventional petroleum additives have solubility problems when added in vegetal oils. Frequently, a dispersant agent has to be used. Amine phosphate compounds are used in biodegradable products, but they are not efficient in petroleum as in vegetable oils. Some anti-wear additives used in vegetal oils reduce oxidative stability when combined with certain antioxidants. These include amine phosphate compounds and molybdenum dialky phosphoridithioate with ZDDC [22].

Gupta et al. [35] presented a review on thermophysical properties of nanofluids, but vegetal oils are mentioned only once. Based on recent literature [29], [36], additives for lubricants could be grouped as in table 1.

Multifunctional additives in vegetal oils are of great interest [33], as they may offer an improvement on several characteristics, especially viscosity and oxidative stability.

| Modifiers of chemical properties | Modifiers of physical properties | Anti-wear and friction modifiers | Extreme pressure additives |
|----------------------------------|---------------------------------|----------------------------------|---------------------------|
| deposit control additives        | viscosity control additives     | metals                           | ZDDP, sulfurized isobutene, fatty oils and olefins, sulfurized synthetic esters, sulfurized fatty oil + olefin |
| anti-oxidation additives         | poor point depressants          | salts (metallic or not)          |                           |
| detergents                       | anti-foaming additives          | carbonic materials               |                           |
| anti-toxicity agents             | dispersants                     |                                  |                           |
| biodegradability promoters       |                                 |                                  |                           |

Nanoadditivation could increase the seizure load in a lubricant, as for instance, the hexagonal boron nitride (hBN) (70 nm) in SAE 15W-40 diesel engine (figure 3) [42]. A concentration of 0.3 vol% of surfactant (oleic acid) was added in order to prevent the sedimentation of the nanoparticles. Ten increments of loading were applied starting from 196 N to 1,570 N, with 10 seconds for every test.

![Figure 3](image-url)  
Figure 3. Wear scar diameter (WSD) and load to seizure evolution for SAE 15W-40 and additized SAE 15W-40 with 0.5 vol. % hBN [42]
Ionic liquids are attractive lubricant additives for their nonflammability, low vapor pressures, structural diversity and reasonable tribological properties. Phosphite binds to aliphatic acid as anion and triethylbenzylammonium serves as a cation, which could be applied as lubricant additives in mineral oil and refined vegetable oils. These additives were added in Arawana 1:1:1 oil (this being the proportion of saturated, mono-unsaturated and poly-unsaturated fatty acids in a combination of vegetable oil). Results demonstrated that these ionic liquids could enhance the tribological properties of tested oil. The chain length and unsaturation of fatty acids are significant in improving the tribological properties of the base oil. [41].

3. Issues related to vegetable oil additivation

The number of additives compatible with vegetable oils, synthetic esters or polyalkylene glycols is small relative to the number of additives compatible with mineral base oils [10].

A package of additives for vegetable oils may contain: detergents, dispersants, anti-corrosion and anti-oxidation agents, anti-foam agents, viscosity modifiers and anti-wear additives, pour-point depressants. It is hard to determine the synergic influence of such a package. But additives also should be both ashless (containing Ca, Na, K, Mg and not other metals) and non-toxic [43]. Among the soaps, calcium-based soaps are considered less toxic compared to other types (e.g., Li-based), and soaps in general are considered less toxic than graphite thickeners [44].

Issues of nanoadditivation of vegetable oils are related to:
- concentration, shape and size of nano particles,
- compatibility with the oil composition,
- chemical and physical stability in time and under the exploitation regime parameters,
- nanoparticle agglomerations, sedimentation, dispersion,
- additive fall-down caused by water that could be present in any lubricant system; water also increases acid formation, seals deterioration, rust generation and wear acceleration. Most bio-fluids are more susceptible to hydrolytic breakage, the result may be acid formation, additive precipitation etc.

A dedicated chapter, “Additives for bioderived and biodegradable lubricants” [22], started by comparing petroleum oils, vegetable oils, saturated esters and polyalphaolephins and concluded that vegetable oils have to be formulated for their individual set of properties.

Reviews on additives for lubricants appear in literature [37], [30], [45], [46], but only few deals with the influence of nanoadditives in vegetable oils, the analysed results being not enough satisfactory as compared to the additivation of mineral and synthetic oils. The addition of nanoparticles to a base oil (mineral, synthetic or vegetable) is a promising approach towards improving certain characteristics, such as friction and wear resistance, thermal and chemical resistance, but literature and reports do not have yet any clear recommendation on how to formulate and to use new additivated lubricants without test laboratory, especially those that could offer data that are compared to the “classical” ones.

Small particles with the size of nanometers, such as graphite [47], boron nitride (BN) [42], natural and synthetic minerals, MoS2 [48], WS2 [49] and polytetrafluoroethylene (PTFE) [50], have been used both as solid lubricants and as additives in lubricants. These particles have a tendency to deposit during storage and use because of their size and their tribological properties remain poor in the presence of humidity and oxygen and, thus, limiting their applications [51]. There have been investigations on the addition of nanoparticles with the typical size in the range of 2–120 nm to lubricants as friction modifiers for efficiently reducing friction and wear. In particular, nanoparticles based on carbon compound, metal, metal oxide, metal sulphide, metal borate, metal carbonate, rare earth compound and SiO2 have been investigated [28], [52], [53] and their tribological performances as friction modifiers are dependent on the degree of crystallinity, size, shape and concentration [30].

There are many studies on neat vegetable oils [54], [55], [13], but the additivation of these lubricant fluids is still at the beginning. A synthetic research work on this subject was done by Zulkifli [38] and the same author gives experimental results for a metal oxide (TiO2) [56]. Glycol was used as solvent. The nanoparticles reduced friction coefficient (COF) up to 15% at high load and improved WSD especially at low load (40 kgf, four ball test) by creating an additional protective layer.
There are two tendencies on vegetal oil additivation:

• to use the same additives as for the above-mentioned oils,
• to formulate new additives, based on particular characteristics of vegetal oils.

Concentration of nano additives in the base oil strongly influences tribological properties, but the optimum values could be hard to be evaluated by theoretical models and the actual influence of additive(s) is determined only by testing. As there are many tribological characteristics that could be affected by additivation and the engineer has to accept a compromise: to optimize a parameter (of high interest for a particular application), to improve others and to make acceptable the induced effects. For instance, the nanoadditives will reduce wear but they could increase the friction coefficient and the temperature in contact. Tests will tune this system approach especially when they are done with parameters in the ranges of actual application.

Alves et al. [57], [58] studied the development of vegetal lubricants with addition of oxide nanoparticles (ZnO and CuO) as additive for extreme pressure (EP), exploring their and base-oil influence on tribological behavior. They considered the additives as for extreme pressure (EP), but it is hard to draw a neat boundary between wear and friction modifiers and EP additives, based on classical literature [29], [36], especially for vegetal-based lubricants, due to their particular physical and chemical behavior in the presence of the additive and under working conditions (load, speed, temperature etc.). The results showed that, with the addition of nanoparticles to conventional lubricant, the tribological properties can be significantly improved. EP additives and reaction substances smoother and form a more compact film on the worn surfaces, which is responsible for the further reduced friction and wear. However, the addition of some nanoparticles in vegetable-base lubricants is not beneficial to wear reduction. A conclusion obtained also by Cristea for adding graphite and graphene in soybean oil [47], [79].

There are researchers that include metal oxides in the category of EP additives [59] but, due to the poor chemical activity on the substrate and to the fact that the layers are not continuous and stable in time, these additives could be treated more like friction and wear modifiers.

Even if many specialists wrote about a smoother and more compact tribolayer formed on the worn surfaces, responsible for friction and wear reduction, recent report and SEM investigations reveal that the tribolayer of wear and friction modifiers is not continuous, very often being a powdery layer of nanosheets, nanoparticles, rolled or not [60], [61] [62].

Manny additives are considered as multifunctional ones as they modify two or more characteristics of interest (for instance, they increase oxidative stability and reduce wear). Ethyl cellulose (EC) could be considered as a multifunctional additive. Delgado [63] reported that adding EC in high oleic sunflower (HOSO) oil and castor (CO) oil make them able to reach stable and non-gel-like blends, with viscosities at 40°C in a large range (62 and 493 cSt) and viscosity indexes into API group III (VI 120). The HOSO/CO/EC blend showed a reduction in friction coefficient at low speed and generated a stable EHD-film at 100°C of around 20 nm, suggesting better boundary properties than HOSO/EC or CO/EC oils. Ethyl cellulose hindered wax crystallization process of these vegetal oil-based lubricants at 5°C. Therefore, the suitable combination of both castor and HOSO oils with EC as multifunctional additive allows for formulating eco-friendly fluids with a wide viscosity range, better viscosity-temperature dependence than many mineral or synthetic oils and excellent boundary lubrication, in applications like hydraulics, metal working, gear transmissions etc.).

The use of vegetal oils as lubricants implies a research on the set of tribological features, including those that can be highlighted on the four-ball tribotester [64], [46]: the influences caused by the nature of the lubricant, chemical and rheological changes, load and speed conditions, the influence of additive(s) nature and concentration, etc. [65], [66].

In the literature, there are reported tests on vegetal oils but the data are far from being comparable and useful for industrial scale applications. The information on the behavior of these oils on the four-ball machine is of interest because it is possible to compare the vegetal oils, whether additivated or not, with those already in use, mineral or synthetic ones [67], [47], [68], [25], [55]. Cermak [69] tested vegetable oils on the four-ball tester in accordance with the American Standard ASTM D4172 and
obtained good values for friction coefficient and diameters of wear scar of 0.53 mm for Cuphea oil and 0.89 mm for Lesquerella crude oil. It is interesting to note that soybean oil had a wear scar diameter higher (0.70 mm) than other oils tested in this study (grasshopper oil - 0.629 mm, cress oil - 0.59 mm).

4. Mechanisms of nano additive for reducing friction and wear

The influence of an additive on the tribology of the contact depends on how the additive evolved in contact as size, shape, structure and chemical composition. A schematic representation of how the additives protect the surface from being worn is given in figure 2.

For instance, a spherical nano additive in contact [70] could keep its shape and acts like a damper or/and spacer between two asperities in contact. But also it could change its shape, becoming flatter when the load increases, protecting a larger surface against rubbing under severe load, the relative motion of surfaces producing a shearing process between additive and surface and not one among asperities [70].

![Figure 4. Types of lubrication: a) lubricant without additives: micro jonctions with cold weld, b) mixt regime with additive that reduces adhesion and abrasion wear (the additive is mechanically fixed on the surfaces), c) coated and/or more flexible nanoparticles minimizing the number or micro-welds and the debris resulted from asperities fractures. [70]](image)

![Figure 5. Photos highlighting two of the steps through which a particle of WS_2 passes into a loaded contact [71].](image)

In 2012, a study by Lahouij et al. [71] shows how the WS_2 particle protects the direct contact between metal asperities (figure 5). The void structure functions as a shock absorber and either the structure collapsed, or the particle was fragmented, it continued to remain between the two solid bodies. The hollow core of the particle was visible and the deformation was large at the beginning of the stress, but as the load increased, the particle behaved like a variable-elasticity spring, the elastic characteristic actually increasing. Then the particle begins to tear or scissor, even to fracture fragments.
The relative size of nanoparticles and asperities is also important in improving the tribological behavior of a contact. A larger additive particle could be trapped in a valley of the texture and could redistribute pressure in a local contact. When the particles are smaller than the profile heights, they agglomerate in the valleys, smoothening the surface, making decreasing the local pressure distribution. Figures 6 and 7 are helpful for understanding how some additive act to protect the solid bodies in contact and, thus, reducing wear [62], [70], [78].

Lee J et al. [72], Lee K et al. [73] and Hwang et al. [74] considered that the addition of nanoadditives in lubricants enhanced the lubrication characteristics as compared to microparticles, but for vegetal oils, the nanoadditivation is still contradictory.

Spheroidal nanoparticles in contact take up some of the load and play the role of very small rollers or ball bearings. Fibrous particles in oils (carbon nano fibers and nanotubes [75], [76], for example) have higher friction coefficients than spherical or close 3D-sized nanoparticles, probably because of the way they fix on the textures in contact and the fact that spherical particles tend to roll and not to be dragged into contact. Fibrous nanoparticles agglomerate more easily than spherical ones and this is why their thickness becomes larger than the thickness of the lubricant film, resulting in an increase in roughness, an embarrassment of the lubricant circulation, especially when entering into contact.

Wu et al. [62] proposed a model that takes into account the additive concentration (figure 6). Although the model was created for TiO2 in water as lubricant, it can be used to explain the behavior of lubricants with other nanoscale particles (metal oxides, carbon materials etc.). The fluid lubrication mechanism with nano additives has been also described in [77], [78], [79].

One or more of the mechanisms for reducing friction and anti-wear mechanisms of nanoparticles in lubricants has been also reported as (figure 7):
- micro-rolling, [62],
- smoothing/leveling [80], [81],
- polishing [73],
- forming protective film [57], [82], [83].

The first two mechanisms have a direct effect on lubrication [73]. In the case of rolling, no chemical reactions occur and spherical or oval nanoparticles are willing to roll, reducing friction.

Shape, size and even size distribution of nanoadditives during functioning of the tribosystem are important factors affecting its durability and performance. The shape directly determines pressures experienced in contact. When starting, a spherical additive will support such a high pressure that it will be flattened, similar to a nanoplatelet and its contact with the solid body becomes planar; under a higher load, the additive could be laminated into a nanosheet. Thus, nanosheets reduce the risk of indenting, scratching or/and deforming the texture of bodies in contact. The problem is that nanosheets
tend to roll instead of remaining laminated on the texture and to form agglomerations of nanorolls that could alter the distance between bodies in contact and to cause friction fluctuation and non-uniform exposure of the surfaces to direct contact and, thus, to generate more intense wear. This aspect was pointed out by Cristea [47], [79] for graphite and graphene in soybean oil and by Cristea et al. [60] for TiO₂ in rapeseed oil.

Despite the general idea discussed several decades ago, the nanoparticles do not form a continuous film on the rubbing surfaces [47], but they intermediate the load transfer and partially transform the sliding into rolling friction.

5. Anti-wear additives and friction modifiers
Anti-wear additives and friction modifiers are used for medium stresses and their protection (not like a film, but like a powdery third body) relies heavily on the adsorption processes and on the regeneration of this intermediate powdery layer, even though particles partially deteriorate or/and they are thrown away from contact during the exploration.

However, due to their poor chemical and physical reaction with the oil and the solid surfaces in contact, nanoparticles have only poor efficiency in oils. This issue could be mitigated by surface modification techniques, for either the particles or the substrates.

A classification of nanoadditives as friction and wear modifiers is presented in Table 2.

Friction modifiers can be classified into two distinct groups depending on the friction reduction mechanism:
- through an adsorbed film,
- by friction with the third body (the additive particles act like spacers, dampers or/and intermediate rolling elements).

The first is generally due to polar molecules having a polar functional radical (alcohols, aldehydes, ketones, esters and carboxylic acids) and a nonpolar terminal group. The polar group of the molecule adheres to the surface with long chains exposed to moving surfaces, reducing friction. They may also have polar elements that may chemically react with the surface to form a protective film. Vegetal oils and animal fats have such molecular structures and, therefore, they have good results in reducing friction.

Dubey [103] studied the effect of particles’ size on the entry in the work zone of the contact and higher the load less is a clear influence and, hence, less nanoparticles are accommodated, but the conclusion for PTFE particles is that they are easily agglomerated and, under compression and shear loads, they may “weld” enough to grow in size and do not entry in contact.

Table 3 presents the diversity of testing conditions, lubricants and additives in order to underline that it is hard to make comparison among results and conclusions and to point out that using the four ball tribotester will be helpful for making a step forward in additivating the vegetal oils.
Table 3. Diversity of lubricant, friction modifiers and test conditions

| Ref. | Friction and wear modifier | Oil Test | conditions | Results |
|------|-----------------------------|----------|------------|---------|
| [95] | ZnO and CuO, 11.71 nm and 4.35 nm, 0.5%wt | soybean and sunflower, by epoxidation reaction | Reciprocating rig (20 Hz mm stroke), ball-on-disk steel ball (570-750 HV, Φ6.0 mm) slides on a softer steel disk (190–210 HV) 10 N, 60 min, 50 °C | biolubricants without additives are slightly more tribologically effective than lubricants with additives |
| [96] | CuO (50 nm, 3.5 Mohs), Al₂O₃ (50 nm, 8-9 Mohs), (0.5, 1.0, 2.0 wt%) | GL-4 (SAE 75W-85), Poly-alphaolefin 8 (PAO8) | four-ball tribotester; ball made of AISI 52100, Φ12.7 mm, 60 HRC | COF decreased in time, more pronounced at 1.0 and 2.0 wt% additive; CuO more effective than Al₂O₃; Al₂O₃ acted as an abrasive (COF increased at all concentrations), with re-agglomeration; CuO has good results at all concentrations, but similar to PAO8; at 2.0 wt% CuO in PAO8, the limit of seizure increases up to 273% optimum concentration 0.8%wt, mass loss is half of the neat oil |
| [89] | Cu 18.2-80.2 nm | SF15W/40 | ball-on-disk GCr15 steel ball (61-63 HRC) and C45 carbon steel disk (hardness 2100 MPa), 15 N, 0.13 m/s, amplitude 5 mm, 20 min. | optimum concentration 7.5 wt% Cu |
| [101] | mineral (China): Mg₅.8₂Al₀.₀₂Fe₀.₀₂Ca₀.₀₂K₀.₀₁(C₁₄Si₄.₂₁O₁₀.₃₆)(OH)₄, Cu (50 nm), 5% oleic acid as dispersant | Diesel engine oil (CD 15w/40) | four ball tester 50 N (Hertz pressure of 1.15 GPa), frequency 10...30 Hz, oscillating amplitude of 1 mm, 30 min | minimum WSD and maximum seizure load for 3%wt ZnO optimal concentration of ZnAl₂O₃ is 0.1 wt% |
| [106] | ZnO (125 nm) 1.0%, 2.0%, 3.0%, and 4.0% | commercial refined base oil (not identified) | four ball tester 30 min, 392 N, 1450 rpm, Φ12.7 mm, 59–61 HRC. | wear resistance and load-carrying capacity raised and COF changed less with 2% Ag in oil |
| [104] | ZnAl₂O₃ (95 nm), spherical: 0.05, 0.1, 0.5, 1 wt.%, ZnO, Al₂O₃ | pure lubricant oil (not identified) | four-ball tester F= 147 N 30 min, 75°C 1450 rpm, oscillating test r, ball-on-disk, tests at 20°C and 100°C, a frequency of 25 Hz, amplitude 1.0 mm, F=100...900 N | 0.8 wt% TiO₂ lubricant has good tribological properties (wear decreases at half) COF dry=0.45, COFwater=0.35 COFwater+TiO₂=0.27 optimal concentration 3% PTFE for minimal WSD |
| [90] | Ag 6–7 nm | low volatile multialkylated cyclopentanes lubricant | four ball tester 100, 200 and 300 N 1000, 1400, 1800 rpm | COF is increasing a little tends to decrease at 1% and heavier loads 0.8 wt% TiO₂ lubricant has good tribological properties (wear decreases at half) COF dry=0.45, COFwater=0.35 COFwater+TiO₂=0.27 optimal concentration 3% PTFE for minimal WSD |
| [47] | carbonic material (black carbon, graphite, graphene) | soybean oil | four ball tester | COF is increasing a little tends to decrease at 1% and heavier loads |
| [78] | TiO₂, 20 nm, 0.2%...8% 0.002...0.08 wt% PEI+10.0 vol% glycerol+water balance | water-based lubricants | four-ball tester | COF is increasing a little tends to decrease at 1% and heavier loads |
| [103] | nano PTFE 0–6% 90–100 nm ZDDP 1...3% | n 150 N API Group II oil | four-ball tester, ball of 12.7 mm, 1450 rpm weld test 60 s | COF is increasing a little tends to decrease at 1% and heavier loads 0.8 wt% TiO₂ lubricant has good tribological properties (wear decreases at half) COF dry=0.45, COFwater=0.35 COFwater+TiO₂=0.27 optimal concentration 3% PTFE for minimal WSD |
Table 3. Diversity of lubricant, friction modifiers and test conditions (continued)

| Ref. | Friction and wear modifier | Oil Test | conditions | Results |
|------|---------------------------|----------|------------|---------|
| [49] | PAO                       | PAO      | reciprocating rig<br>Pressure 1.12 GPa,<br>lubricant temperature 100°C,<br>0.5 Hz, 8 h, 14400 cycles | Tribological properties of nanoparticles enhanced when ZDDP is present. The-anti-oxidant properties of ZDDP protectWS2 from oxidation.<br>PTFE+ 1% hNB |
| [50] | PTFE (12 μm) + hNB (70 nm), 0–4% each; dispersant (1 wt%) and petroleum ether PIBSI (1%) | Group III<br>PTFE (12 μm) + hNB (70 nm), 0–4% each; dispersant (1 wt%) and petroleum ether PIBSI (1%) | four ball tester<br>weld test<br>wear test 392, 588 and 784 N | max. non-seizure load and minimum WSD at 0.2% treated graphene oxide |
| [88] | graphene oxide three types<br>0.2 wt. % to 0.4 wt. % | rapeseed oil | four ball tester<br>seizure test 1760 rpm 0.67 m/s, for 10 s.<br>wear test 98 N; 196 N; 294 N; 392 N | |

The extreme pressure additives are chemically bonded to the rubbing surfaces, especially when the temperature reaches the threshold of additive reaction with the metallic surfaces. The addition of ZDDP additive in soybean oils effectively protected the rubbing surfaces, but it showed no clear trend on the friction coefficient. For epoxidized soybean oil and high-oleic soybean oil, the temperature and the additive interactions predominantly affected the wear scar diameters. The additive tends to improve stability and to have a less dependence on speed and temperature, but not a consistent reduction in wear scar diameter [110]. Similar results were obtained by Cristea [47] with nano friction modifiers (black carbon, graphene and graphite) in a degummed and refined soybean oil.

Figure 5 exemplifies the diversity of shape and size of wear improvers and friction modifiers.

![TEM image of Ag nanoparticles](#a)

![Phyllosilicate natural mineral serpentine. 1 to 5 μm](#b)

![La(OH)₃ nanoparticles 50 nm](#c)

**Figure 8.** Diversity of size and shape of nano additives for lubricants.

Zareh-Desari [32] studied the influence of adding SiO₂ and CuO (0.3...1%) in soybean and rapeseed oils, containing various concentrations. Silica nanoparticles (SiO₂) have appropriate dispersivity and stability even in high volume fractions [87].

Padgurskas et al. [91] analyzed the influence of different metal nanoparticles (Fe, Cu, and Co) on a mineral oil (SAE 10) and they exhibit different behavior when added to this oil. Cu particles possess the most effective wear resistance characteristic. They reported that a mixture of nanoparticles is more effective than using them separately.

Ma [90] added Ag nanoparticles highly soluble in non-polar and weak polar organic solvents as a synthetic alkylated cyclopentane oil (having high decomposition temperature and very low vapor loss) and improved wear performance and load-carrying capacity, with low effect on friction (figure 9). During the friction process, Ag nanoparticles were deposited on the friction pair surfaces to form metal Ag boundary film, with low shearing stress and contributed to prevent the steel-to-steel contact.
from severe adhesion and abrasion.

**Figure 9.** Friction coefficient (a) and wear volume (b) of steel/steel contact lubricated with synthetic alkylated cyclopentane oil (MAC) base oil and containing 2% Ag nano particles at 100 °C for 1 h [90].

Wu et al. [78] analysed TiO$_2$ and CuO behavior as nanoadditives in lubricant oil. The addition of two different nanoparticles in oil decreases its friction (CuO performed better than TiO$_2$). In addition, both exhibited uniform dispersion and distribution in the base oil. Figure 10 presents details on the wear scars on balls tested with rapeseed oil with particles of TiO$_2$, (1 wt% TiO$_2$), at $v=0.69$ m/s [60] and one may notice that the dispersion on the surfaces are non-uniform and some particles agglomerate, becoming of micronic size.

![Wear scars with particles of TiO$_2$, after testing the rapeseed oil with 1% TiO$_2$, at $v=0.69$ m/s [60].](image)

**Figure 10.** Wear scars with particles of TiO$_2$, after testing the rapeseed oil with 1% TiO$_2$, at $v=0.69$ m/s [60].

The anti-wear behavior of oxide nanoparticles depends on the lubricating base oil. They do not show good anti-wearability when combined with epoxized vegetable oil, like sunflower and soybean oils, because of chemical nature of these oils on film formation due to polar groups that adhere to surface. In this case, nanoparticles have a third body behavior, increasing friction. ZnO reduces friction and wear when introduced in a mineral oil. Synthetic oil has its tribological properties improved with addition of CuO [30].

Solid lubricants are added in oils with the purpose of reducing friction and wear. This group of friction modifiers includes carbon materials (fullerene, nanotubes, graphite, graphene etc.), but also molybdenum and wolfram sulphides, fluorinated polymers, such as PTFE and perfluoropolyalkylethers [30]. Solid lubricants (micro or nano) also help in situations where sliding surfaces have a more rough texture, “leveling” the profile of both surfaces. They are also recommended for reciprocal movements (in the case of the piston ring), producing a reduction in wear.
It is added to lubricants that come into contact with surfaces with which EP additives can not chemically react, such as polymers and ceramics and some of their composites [36].

The lubrication mechanisms of nanoparticles as friction modifiers include three types of friction [107]:

- rolling friction: spherical nanoparticles act as micro or nano ball roller bearings between triboelement surfaces, under light load conditions,
- sliding friction: nanoparticles serve as spacers and eliminate direct metal/metal contact between the asperities of the two triboelements, under higher load conditions,
- rubbing with the third body: exfoliating nanoparticles and their outer layers gradually transfer to the surface textures, providing easier friction under high load conditions, when the third body may be considered a mixture of oil, nanoparticles and wear particles.

The use of nanoparticles as lubricant additives is a top issue of research in the last decades [30], [70].

Jayadas et al. [64] have calculated the advantage of using additives in oils, based on the results of the shear rate and the temperature influence on the viscosity of the additivated lubricant. Wu et al. [62] reported increased load capacity for the nanoadditivated lubricants. Many studies were based on a single concentration of the additive. The effect of varying viscosity due to nanoparticle concentration is difficult to model and, therefore, tests become relevant.

6. Carbon nanoparticles as additives in lubricants

The use of nano-carbon materials is more recent - the last decade. Specialists divide nanocarbon materials into four classes, depending on carbon allotropy: zero dimension (fullerene, but also black amorphous carbon), single-dimensional or 1D (carbon nano wires and nano bars), two-dimensional or 2D (graphene [86]), three-dimensional or 3D (diamond powders).

For the time being, graphene friction patterns and data obtained at AFM are contradictory [86]. Tribotests that allow for more pertinent comparisons and proximity to actual tribosystems are few and, therefore, the influence of adding graphene as oil additive has to be tested. Graphene is considered a rising lubricant [86]. In spite of the efforts of developing research for existing and future applications, their tribological potential as a lubricant remains relatively unexplored. Very high chemical inertia, good strength and the ability to crack easily between platelets or very smooth surfaces are favorable attributes for a very good tribological behavior.

Lin et al. [108] studied the stability of micro-graphene plates in oil and tested as dispersants: sodium dodecyl benzene sulfonate, stearic acid, dodecyl trimethyl ammonium chloride, oleic acid, sorbitan monooleate and polysorbate. They concluded that, from of all these substances, stearic acid and oleic acid are the most suitable dispersants. The optimal concentration of modified graphene was 0.75 wt%, reporting an improvement in wear and contact loading capacity. The results were superior to the addition of natural graphite flakes in the same oil.

Xiao and Liu [27] compared various types of 2D nano additives. Materials with layered structures, such as graphite and MoS₂, are applied as solid lubricants. Two adjacent layers of these structures are bonded by weak van der Waals forces, leading to low shear strength, which allows adjacent layers for sliding easily against each other under shear force, providing the friction reduction, even in the presence of a fluid.

As compared to conventional organic lubricant additives like molybdenum dithiocarbamate (MoDTC), zinc dialkyldithiophosphate (ZnDTP), and zinc dialkyldithiophosphate (ZDDP), carbonic nanomaterials (see examples in figure 11) are superior in two aspects:

- they exhibit good performance in reducing friction and wear, but the authors’ opinion based on recent papers [47], [79], could point out that is true for moderate regimes (figure 12),
- significantly lower toxicity than some organic and inorganic additives, making them attractive for environmentally restricted applications.
Figure 11. Different carbonic materials used in soybean oil as additives [47]

Figure 12. Maps of the rate wear of WSD, w(WSD), for soybean oil base lubricants, additivated with 1wt% nano additive (carbonic materials, tested 1 h on a four ball machine) [47]

The downward trend of w(WSD) had a higher gradient for lubricants with 1% nano additive, which would recommend further testing for more severe regimes, where additives are likely to better protect the surface of the contact. The wear rate of WSD is calculated as:

\[ w(WSD) = \frac{WSD}{F \cdot L} \]  \[ \text{[mm} / N \cdot m \] \]  \[ (1) \]

where WSD is the wear scar diameter average for a test [mm], F - the load applied on the four balls [N], L - the sliding distance [m].

Although micro-scale diamond particles are used for surface superfinishing, it has been found that at the nano level, these particles act on the principle of bearings, like roller balls between the two surfaces in sliding. The results on nanodiamonds are contradictory [81].

Lee [72] studied nanographite in a mineral oil for transmission (220 cSt at 20 °C) (Supergear EP220, SK, Korea), but this oil also had EP additives. The average graphite size was 55 nm. The tested concentrations were 0.1 wt% and 0.5 wt%. The alkyl aryl sulfonate was used as a dispersant. Agglomerations of particles acted as a contaminant and increased the risk of generating more abrasive wear by passing agglomerations through the contact and "falling" (continued slipping with local shock in contact).

Graphite is effective in high temperature and high load applications. Similar lubricants, such as MoS2, will rapidly oxidize when working temperature reaches 760-1200 °C, although MoS2 has a better lubricating capacity. Graphite is such a good solid lubricant due to the lamellar plate structure, composed of planes of hexagonal carbon atoms, with weaker van der Waals forces holding together the planes [109].
7. Conclusions
From the studied literature, there is a tendency for research on additivation of vegetal oils, especially for lubrication. Addition of nanoparticles may improve tribological properties of vegetal oils. Friction is not always reduced, but the increase in friction coefficient is acceptable as it is accompanied by a substantial reduction in wear. Most tests are done on four ball machine, pin/ball-on-disk and reciprocating tribotesters. Attention should be focused on the dispersion of nano additive and the selection of dispersant.

The reported results are still inconclusive and the applications of these oils are based more on market inertia or on the practical experience of users.

Despite the advantages of nanoparticles as oil additives, as analysed and summarized in this paper, there are also some challenges hardwired to their applications, which could potentially form future research:
- to prepare and maintain homogenous mixtures of nanostructure particles and oils. Strong van der Waals forces between the particles cause them to aggregate in solutions; therefore, various modification techniques should be investigated for the stabilization of nanoparticles in vegetal oils to produce lubricants, physically and chemically stable,
- to test under adequate conditions, closer to the considered future applications,
- to report results in a manner that allow for comparing data and translating them to the actual tribosystems.

The conclusion is that additivation of vegetal oils is still at the beginning as the reported results are not so efficient as compared to the additivation of classical alternative - the mineral oils and even less, as compared to synthetic oils. But research must be continued as these vegetal oils become an actual resource for lubricants base-stock.

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