ARE BIOBASED LUBRICANTS FOOD FOR MICROBES?

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Favored by legislators for their sustainable properties, biobased lubricants are ideal for applications where environmental sensitivity is crucial. Chemical engineers Chrysovalanti Tsesmeli and George Dodos offer us an insight into their Achilles heel – microbial contamination.

Interest in renewable lubricants has increased in parallel with a wider concern for the protection of the environment and the sustainability of the lubricants industry. There is now a fast-growing market for high added-value biobased lubricants formulated with materials such as mono and polyol esters derived from plants and animal fats.

Their use across a broad range of applications is highly encouraged by policymakers due to their non-toxicity, biodegradability and renewability, which in turn leads to the reduction of their carbon footprint during production.

A wide palette of biobased esters is available to formulators these days, ranging from simple monoesters to complex ones, while the degree of saturation varies from purely unsaturated to almost fully saturated.

Mandated Use

Consumption of biobased lubricants in Europe is estimated to be about 100,000 metric tons per year, largely in total-loss and high-risk industrial applications, such as rail grease and hydraulic fluids. However, this quantity could quadruple over the next decade under a potentially binding legislative framework for supporting biobased lubricants. This could be done by mandating the use of such products in environmentally sensitive areas, for example.

National and European Union-wide eco-labelling schemes are already in place for commercial biobased lubricants and have the potential to further promote the use of these products. Furthermore, a significant step was made by the European Committee for Standardization, known as CEN, in 2016 when it published the European standard EN 16807. This standard designates the minimum requirements for renewability, biodegradability, toxicity and technical performance of biobased lubricants.

Apart from their environmental benefits, biobased lubricants possess several advantageous performance characteristics – higher viscosity index, lubricity and flash point – compared with conventional oils. However, their main weaknesses are largely related to their chemical structures. Oxidation and thermal stability, affinity to water and performance at low temperatures are the most notable.

Another issue that should be taken into consideration is that their chemistry bears resemblance to other types of renewable petroleum

Table 1: Physical Properties of Tested Fluids

Type	Isopropyl oleate	Ethylhexyl oleate	TMP trioleate	TMP tricaprilate	Pentaerythritol Fatty Acid Esters	Blown vegetable oil	Group I mineral oil
Chemistry	Mono-ester (U)	Mono-ester (U)	Mono-ester (U)	Tri-ester (S)	Mono-ester (U)	Tri-ester (S/U)	H/C
Kinematic viscosity at 40°C, centistokes	5.5	8.8	47.5	19.2	5.5	146.4	30.5
Viscosity index	208	188	191	144	208	177	99
Acid value, milligrams of KOH per gram	0.28	0.42	0.60	0.15	0.28	1.24	0.06
Oxidation stability, RSSOT, minimum	11	12	14	254	11	80	1450
Inhibitory potential against Gram-positive bacterium	+	+	-	-	+	+	-

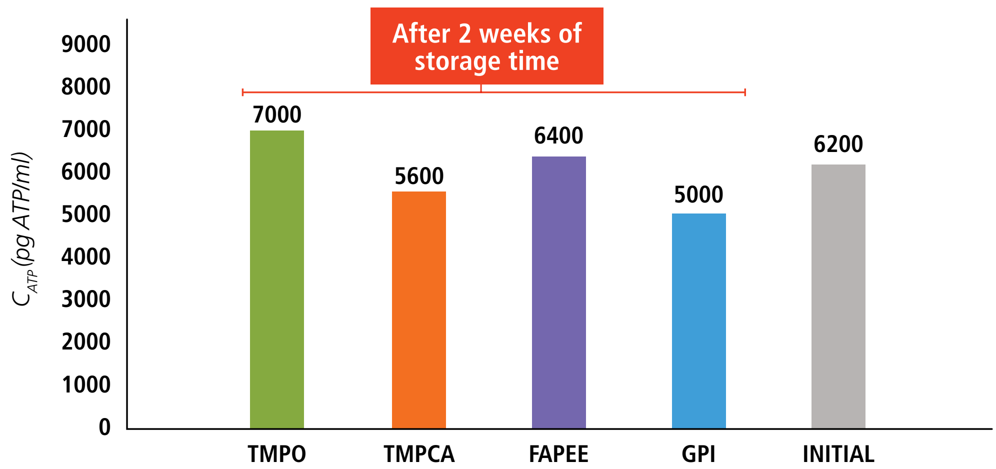
S: Saturated U: Unsaturated

products, such as biodiesel. Biodiesel consists of fatty acid methyl esters, known as FAME, which are oleochemical derivatives that can be susceptible to microbial contamination due to their chemical composition and hygroscopic nature, or their tendency to absorb moisture from the immediate environment. Many incidents associated with diesel fuel biodeterioration have been reported worldwide and have been attributed to the presence of FAME.

Bugs in the System

Microbial contamination of fuels and lubricants is not a new phenomenon. It was demonstrated in the late 1890s that even petroleum hydrocarbons could be "attacked" by microorganisms. Another widely reported issue is the microbial contamination of metalworking fluids, in which water is deliberately added

Figure 1: Microbial Activity in Aqueous Phase of CWMs



to the work piece as a coolant. Some of the undesirable effects of this kind of contamination include unpleasant odors, oil degradation, fouling of filters and equipment failure.

Based on the experience of FAME, it is therefore interesting to examine the behavior toward microorganisms of oleochemical esters that are commonly used in biolubricant formulations and how their characteristics may be affected in case of microbial proliferation.

In order to get a picture of the microbial stability of different types of biobased esters, a number of commercially available products were evaluated for their susceptibility to microbial contamination. Table 1 shows the main physical properties of the tested fluids.

The examined oleochemical esters were two monoesters (isopropyl oleate and ethylhexyl oleate), a monounsaturated tri-ester (trimethylolpropane trioleate or TMPO), a saturated tri-ester (trimethylolpropane tricaprylate or TMPCA), a tetra-ester (pentaerythritol fatty acid esters or FAPEE) and an oxidized, or "blown," vegetable oil. An API Group I mineral base oil was used as the reference fluid.

Initially, the inhibitory potential of the examined biobased esters against the growth of Gram-positive bacteria Bacillus stearothermophilus was assessed. (Gram-positive denotes the structure of a bacterium's cell wall making it easier to kill.)

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According to the results presented in the last row of Table 1, the monoesters and the blown vegetable oil did not promote the growth of microorganisms. The inhibitory activity of the tested monoesters against vegetative bacteria is attributed to the alleged disinfectant efficacy of isopropyl alcohol and ethyhexyl moiety, whereas in the blown vegetable oil might be due to the presence of epoxy and/or peroxy functional groups.

Meanwhile, the rest of the esters, as well as the reference mineral oil, were not a limiting substrate and thus the bacteria were able to proliferate under the conditions of the test.

Following the above screening, those biobased esters that did not inhibit bacteria growth – TMPO, TMPCA and FAPEE – were further analyzed for their proneness to microbial proliferation by setting up "challenged" and control microcosms, meaning small scale systems that simulate real-world conditions. These comprised an organic phase (the lubricant) and an aqueous phase

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(the water) underneath. The challenged microcosms (CWM) were contaminated with an inoculum of known initial microbial activity, whereas the control microcosms (DWM) were in distilled, sterilized water. The microcosms were stored for two weeks under stable temperature and humidity conditions.

The evolution of the microbial growth in the aqueous phase of the CWM was determined by measuring adenosine triphosphate bioluminescence (see Figure 1). ATP is the primary energy source for all living organisms and allows for the detection of the number of metabolically active cells in a sample.

In a system where the aqueous phase is separated from the organic phase, it is a general practice that the former is examined first in order to check for good control of the testing system. Microbial proliferation takes place mainly in the interface between the oil and water, where the availability of nutrients and oxygen is optimum. As a result, the formation of an intermediate biofilm can be observed.

The presence of microbial communities in the organic phase is considerably lower compared with the activity in the aqueous phase underneath it.

In this comparative assessment, all of the examined biobased esters were found to be more susceptible to microbial contamination than the conventional base oil. The monounsaturated biobased lubricant TMPO was found to be a more favorable substrate to microbes than either the saturated TMPCA or the FAPEE, since at the end of two weeks' storage, microbial growth had increased by 15 percent.

Cultured viable microbial activity in the organic phase was also assessed (see Figure 2). Usually, the presence of microbial communities in the organic phase is considerably lower compared with the activity in the aqueous phase underneath it. However, the detection of higher levels of viable microorganisms means that a corrective action should be undertaken in such a system. Such actions may include treatment with a proper microbicide, cleaning of the system and filtration of the contaminated organic phase.

Regarding the effect of microbial activity on the quality parameters of the biobased esters, the change in acid value and oxidation stability was determined at the end of the storage period. In all cases, oxidation stability of the esters was not substantially affected throughout this period, either by the presence of water or the activity of the microorganisms. Meanwhile, the impact on the acidity of the esters is noticeable (see Figure 3).

It is worth noting that the relative

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Figure 2: Microbial Activity in Organic Phase of CWMs

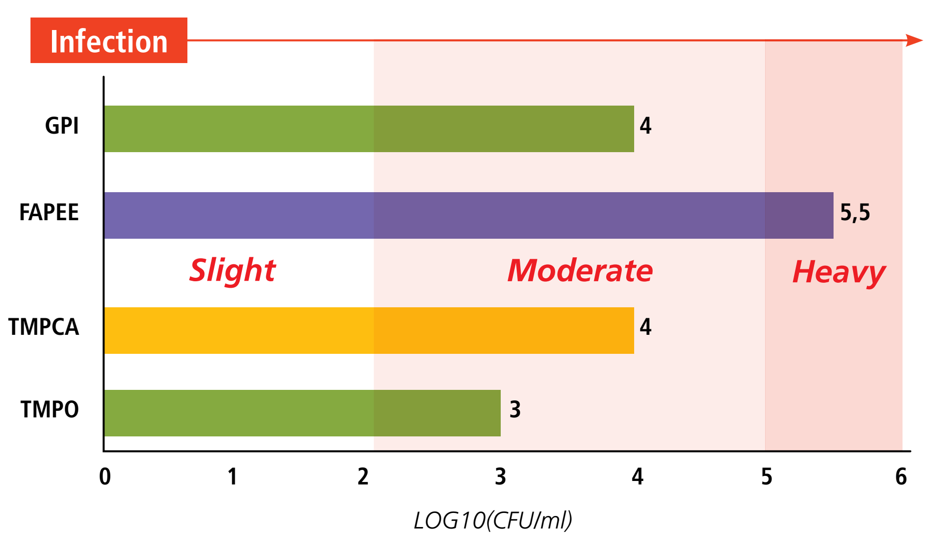
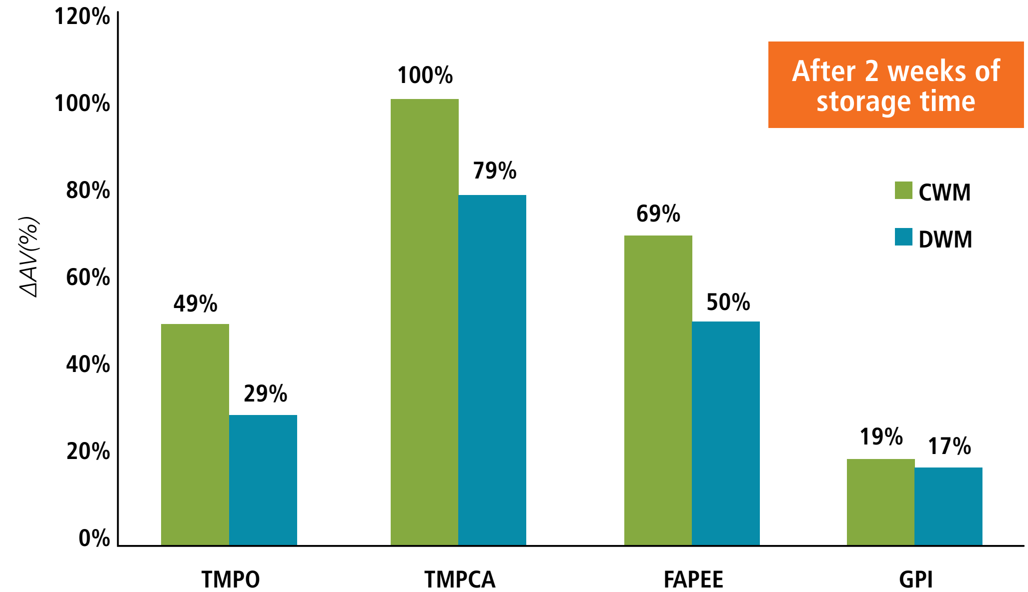


Figure 3: Increase of Acid Value in Organic Phase (%)



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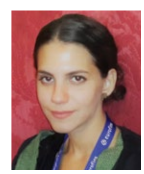
increase of the acid value was considerably higher in the contaminated microcosms compared with those that contained a non-inoculated aqueous phase DWM. This implies that microbial activity has the potential to adversely affect this quality parameter of a biobased lubricant.

Every coin has two sides. In the case of biobased products, their inherent environmental benefits (higher biodegradability and lower toxicity) can be accompanied by undesired biodeterioration issues that may be experienced during their service life. The current data suggest a number of biobased esters that are commonly employed in the formulation of biobased lubricants have the potential to support the proliferation of an active biomass.

Since the presence of water is a critical parameter for microbial growth, as long as it does not infiltrate the system and good housekeeping measures are employed, symptoms are unlike to evolve. However, there are certain applications where the presence of water is inevitable – either intentionally or not – such as in metalworking fluids, turbine oils and in offshore activities. Therefore, operating conditions along with monitoring during application should be optimized in order to keep systems inhospitable to microorganisms.

Another prospect could come from additives. Fully formulated lubricants contain a series of performance improving agents that depending on their chemistry can interfere with microbial activity. For example, in a previous work, it was shown that certain phenolic-type antioxidants have the ability to suppress microbial growth in biobased esters. In any case, the projected increase in biolubricant products should take into consideration the different chemistry and characteristics compared with conventional petroleum based mineral oils. Their biodeterioration potential and cost-effective control should be put in the equation whenever the conditions appear auspicious. ◻



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