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AN stle PUBLICATION | JANUARY 2025

BIOBASED ADDITIVE ADVANCEMENTS in Lubricating Products

Biobased and sustainable additives are shaping the future of lubrication technologies.

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Biobased and sustainable additives are shaping the future of lubrication technologies.

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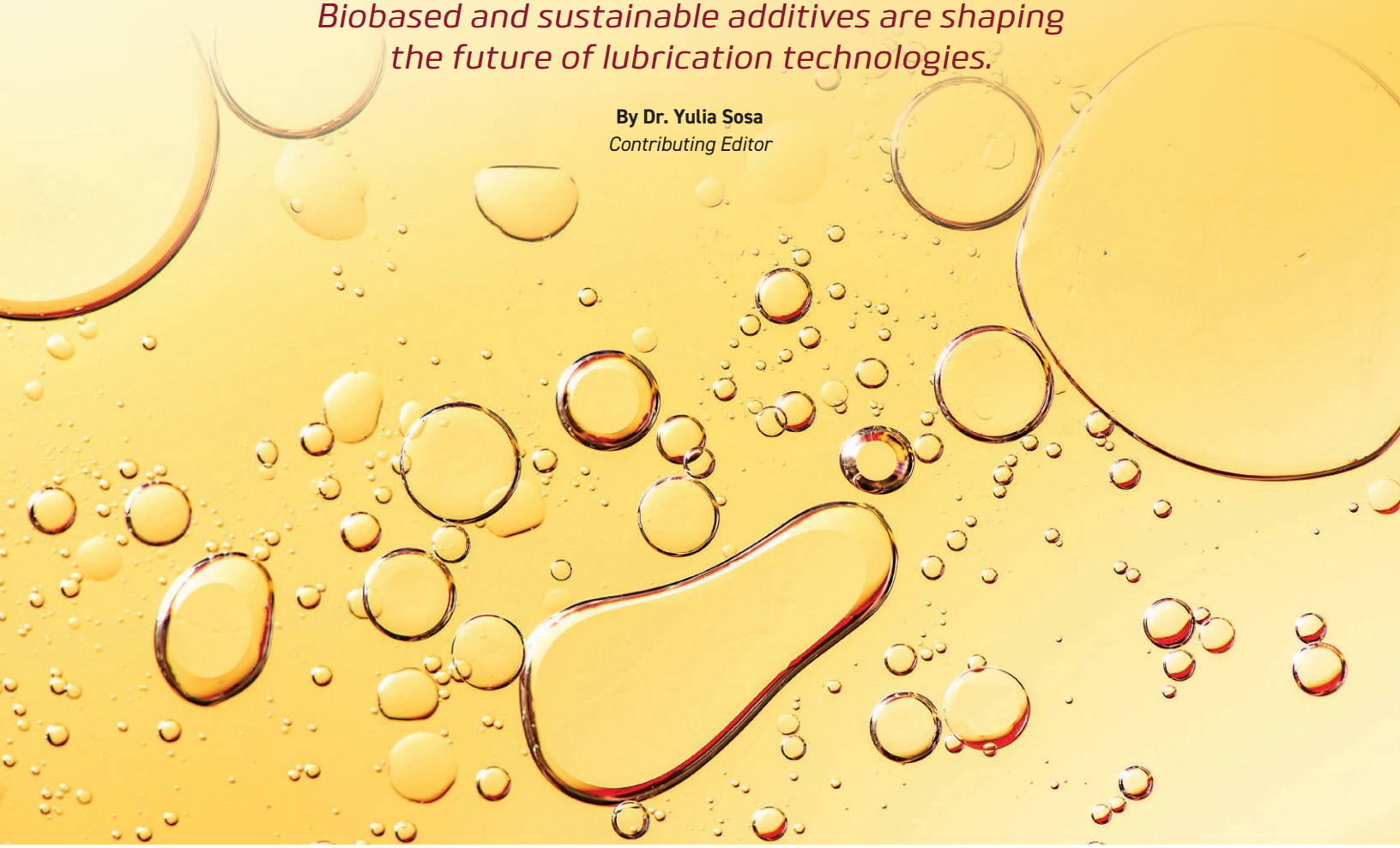

KEY CONCEPTS

Additives used in lubricating products are becoming more regulated, especially from a biobased, environmentally friendly perspective.

Globally there are a limited number of biobased additives available.

Performance, compatibility, cost and global availability are key requirements from lubricant marketers to implement biobased additives into their product portfolios.

With rising environmental conservation efforts and the depletion of petroleum resources, there has been a growing interest in developing lubricant additives derived from bioresources. This article explores the increasing importance of biobased additives in lubricants within the fields of tribology and lubrication technology. It will examine recent advancements, challenges and upcoming prospects related to the incorporation of ecofriendly additives into lubricant formulations. Topics will cover the motivations for transitioning to sustainable lubricants, such as regulatory pressures and environmental issues, as well as the quest for better performance characteristics.

Overview

Biobased lubricants offer numerous economic, environmental, safety and health benefits over petroleum-based lubricants. In order to take full advantage of these benefits, the biobased lubricant must be formulated using a biobased base oil and biobased additives. Currently, there are a handful of biobased base oils in the market from which the formulator can select to blend biobased formulations.[1]

Dr. Martin Greaves, chief technology officer, VBASE Oil Co., concurs: "Most additives used in lubricant formulations today are derived from petrochemical feedstocks." He adds: "However there continues to be a growing interest in additives derived from oleochemical

sources particularly biobased additives designed to function on surfaces such as friction modifiers, antiwear additives and corrosion inhibitors. Long-chain fatty acids, their ester derivatives or functionalized esters are commonly used as a friction modifier in engine oils, transmission fluids and hydraulic oils where reduced friction losses can lead to fuel efficiency benefits."

"Many greases already contain biobased components," shares STLE member Dr. Erik Willett, president, Functional Products Inc. He continues: "12-hydroxystearate is a derivative of castor oil for lithium 12-HSA and calcium 12-HSA greases and complex greases. Other thickeners may utilize fatty acids like stearic acid or small carboxylic acids like acetic acid, which can be sourced from triglycerides and fermentation, respectively. Carboxylic acids also can be synthesized so it is important to ask suppliers about the synthetic route of their raw materials, or test for biobased carbon with methods like ASTM D6866. Some esters like adipates are entirely synthetic and have quite high carbon footprints so don't make assumptions."

Willett explains: "Long-chain fatty acids and esters are great friction modifiers in lubricants and can be used to make surfactants for metalworking fluids. Chemical derivatives of fats using sulfur, phosphorus, nitrogen, boron or other elements can produce a wide array of antiwear (AW), extreme pressure (EP), corrosion inhibitors (CI) and more. Large fatty feedstocks, versus synthetic olefins, can dilute the concentration of those sulfur/phosphorous/nitrogen functionalities and may result in tradeoffs of AW/EP/CI performance, lubricity and solubility."

Willett adds: "Most of the biobased development on the market that I see is biobased base fluids. 'Base oil' has become a very loose term since esters, polyalphaolefins (PAOs), polyalklene glycols (PAGs) and other stocks are no longer 'oil.' Biobased formulations may be 90%-99% biobased base fluid with 1%-10% conventional additive technology including EP, AW, antioxidants and demulsifiers/defoamers. The largest piece of the lubricant market is the base fluid, and if a low-cost solution which works for everyone can be found then that solves 90%-99% of the problem."

He says: "These base fluids can enable additive-like improvements when used as co-base stocks in a formulation. Greater than 25% by weight of a co-base stock is a general rule of thumb to begin to see significant effects on stability, solvency, viscosity and low/high-temperature fluidity. Fatty esters can help improve AW and EP properties as a co-base stock, too. Many full synthetic formulations with PAO already use 5%-10%wt of an ester to improve the solubility of additives."

> 'The ideal case is to create high-performance lubricants that contain both sustainable (biobased) additives as well as sustainable (biobased) base oils.'

Technical considerations

Greaves shares that there are some key technical considerations in the development and production of biobased additives for lubricants. He says: "Companies aiming to develop new biobased additives must demonstrate that these products can match or surpass the performance of petrochemical-based additives, which have been reliably used in formulations for decades. Additionally, these biobased additives may need to offer superior environmental benefits, such as low ecotoxicity, non-bioaccumulation, high biodegradability and a high bio-carbon content, depending on their intended application. Securing stable and sustainable feedstock sources for production also is a crucial consideration."

Willett also shares a list of key technical considerations: "Hydrolytic stability and often thermoxidative stability are key, depending on the application. Secondary considerations are seal swell properties since highly polar biobased materials can compromise seals or attack paints/coatings in and around the mechanical system. If polarity or molecular branching is too high, then the additive may simply be insoluble in many conventional base stocks and will drop out over time." He continues: "On a metal surface, molecules of different size and chemical affinity all compete to adhere to the metal. This includes base fluid and additive molecules. Biobased molecules can be bigger and/or more polar than conventional technology, which will cause the chemistry to interact differently at the site of wear or corrosion on metal surfaces than conventional chemistries. The ratio and weight% of additives in the formulation may need to change or entirely new chemistries may be needed to obtain the desired performance."

STLE member Dr. Larry Beaver, vice president, research and development, RSC Bio Solutions, shares that from a lubricant developer's perspective, there are also some key considerations when selecting and integrating biobased additives into lubricant formulations: "In an ideal world, performance is always key. The reality is often different, and lubricant performance, formula cost and raw material availability must be optimized. In every formulation, the final requirements of the customer must be clearly known and met, while balancing performance and cost. We are in a post-COVID-19 world where limited raw material availability is still a very real factor. For instance, a tight isostearic acid supply has negatively impacted the supply chain for ester-based friction modifiers and base oils. Availability impacts the formulators' choices when evaluating new or selecting existing raw materials. The cost of these raw materials also fluctuates, sometimes widely during the year as growing conditions impact the availability of the plant-based commodity oils used to create many of the biobased additives. Product line rationalization at additive suppliers and/or regulatory action can also limit or entirely eliminate additives from a formulator's portfolio."

Beaver says that it is possible to create biobased lubricants with conventional additives that meet sustainability and environmental requirements, and it also is possible to create non-sustainable lubricants using biobased additives: "The ideal case, and one for which our industry strives, is to create high-performance lubricants that contain both sustainable (biobased) additives as well as sustainable (biobased) base oils. These formulae must compete in the marketplace with established, top-of-the-line conventional mineral oil or synthetic

lubricants. We must not lose sight of the fact that customers are no longer willing to sacrifice performance solely to meet environmental or corporate sustainability goals. Customers will not pay three times as much for a biobased product that works just as well as a conventional lubricant. The value proposition balancing cost and performance with sustainability must be a compelling factor considered during the formulation development process."

Environmental compliance is a critical factor to consider. He adds: "Requirements set by the U.S. Environmental Protection Agency (EPA), OSPAR (Oslo and Paris Conventions), Blue Angel, Ecolabel and Swedish Standard as well as the Lubricant Substances Classification (LuSC) list can provide direction to formulators who wish to market the most sustainable lubricants to the widest possible markets. These regulatory and certification organizations set requirements and/or grant approvals only after considering a wide variety of health, safety and environmental impacts of the raw materials and/or final lubricant formulations."

Overall, from Beaver's experience, there are some key performance attributes and benefits of biobased additives in lubricants, and how they compare to traditional petroleum-based additives. He says: "Key performance attributes are generally related to stability in the formulations in-service and lubrication performance advantages when compared to petroleum-based additives. Many lubricants are used in harsh environments, often with exposure to high moisture levels under high-stress conditions. The marine and wind power segments are placing increased performance and stability demands on next-generation lubricants, and the additive industry and formulators face a real challenge in producing sustainable options to address the hydrolytic and shear stability as well as the new EP and AW performance requirements of these demanding applications."

In recent years the adoption of biobased additives has evolved in the lubricant industry.

Adoption of biobased additives

In recent years the adoption of biobased additives has evolved in the lubricant industry. Willett shares some main drivers and challenges: "The easiest implementation will be biobased sources of existing additives." He explains: "Events like the COVID-19 era shortages, recent changes in toxicity labeling of key raw materials and the shift from lithium to alternative greases have refreshed our willingness as an industry to consider alternatives. Fatty acids and their derivatives are common biobased feedstocks but can't make everything. Novel feedstocks via lignin derivatives, gasification of biomass or fermentation could produce more complex structures like phenolic and aminic antioxidants. It will be one challenge to recreate core industrial chemistries from biomass, but doing so at a competitive price will be an even bigger challenge."

He also warns: "There will be switching costs. The chemical industry has evolved over hundreds of years to produce our 'conventional' technologies in a highly competitive, cost-sensitive market. Biobased feedstocks may require new plants or retrofitting existing infrastructure. The lubricant industry itself might not justify these large expenses, which means smaller, more boutique operations will arise which won't have the economy of scale to price out against what already exists. It will take investment and policy to catalyze this, but policy can cut both ways. The bio-diesel market also has had pushback from policies designed to prevent edible oils from being taken out of the food supply."

Greaves says that the appetite within our industry for biobased solutions has never been greater as industries look toward a future beyond petroleum oil. "Biobased additives that can demonstrate excellent functionality and environmental performance, versus petrochemically derived alternatives, have a promising future. Initiatives such as the Vessel Incidental Discharge Act (VIDA) and the EU Ecolabel favor lubricant solutions that have a low environmental impact," Greaves says.

Innovation

When it comes to innovation, Greaves states that ester chemistry remains a fertile exploratory area for the development of sustainable lubricants and biobased additives. "There are novel ester products that have recently been introduced, which offer low ecotoxicity, non-bioaccumulation, high levels of biodegradability and a high bio-carbon content. The inclusion of high levels of oxygen in their molecular architecture leads to excellent film-forming behavior such as high load-carrying capacity and friction control, which can lead to energy efficiency gains in equipment. The key functional benefits are being explored in equipment trials. A further distinguishing feature is their high volumetric heat capacity indicating they have the potential to improve heat management in equipment."

He adds: "The science of biotribology, ▶

especially the study of natural lubricating molecules, offers a rich field for research and industrial application. For instance, human joints, which are lubricated by synovial fluid, exhibit remarkably low friction coefficients. The glycoprotein Lubricin plays a key role in this process by providing exceptional boundary lubrication. Understanding and leveraging these natural mechanisms could lead to significant advancements in our industry."

Greaves explains: "Ionic liquids have attracted considerable research interest over the past two decades. Initially, challenges with oil solubility were a major obstacle, but recent breakthroughs have led to the development of new molecules that are oil soluble. Among these, phosphonium-phosphate and ammonium-phosphate ionic liquids have shown exceptional performance as AW additives in ester-based fluids, outperforming conventional options. Additionally, these new additives have favorable ecotoxicity profiles, making them a more environmentally friendly choice compared to some traditional chemistries. However, a significant challenge remains in manufacturing these additives cost effectively. Addressing this issue is important for making these advanced ionic liquids commercially viable."

Willett comments on innovation: "The bulk of biobased formulations are based on natural triglycerides (vegetable oil) or synthetic esters, with some biobased hydrocarbons. Base fluid producers are able to invent new fluids that achieve exceptional performance in certain areas, but trying to make a single base fluid that does everything will hit a fundamental limit of material science." He shares the example of esters:

- Unsaturated esters like vegetable oils are the lowest cost option but have poor thermoxidative stability.
- Using saturated fatty acids like C16-C18 improves the resistance to heat and oxidation, but now the low-temperature properties suffer, and the pour point is too high.
- Using short-chain saturated fatty acids like C8-C10 improves the cold flow, but now the cost has increased and the flash point at high temperatures has suffered.

He continues that the producer must settle on a compromise between these competing mutually exclusive properties. "There is no perfect base fluid that does what you need it to do right out of the drum, which is why the additive markets exist," Willett says. "Biodegradability versus viscosity also is a key problem that needs to be addressed. Making high-viscosity biobased lubricants with good biodegradability is a challenge. The higher molecular weight and branching needed for high viscosity fluids also inhibit the ability for nature to break down the molecule. One approach is to use a small weight% of very high viscosity material as an additive to increase the viscosity to the target ISO or SAE viscosity grade without making a change in the overall biodegradability or biobased content of the base fluid."

He adds: "There are a lot of exciting but prohibitively expensive materials coming onto the market. Innovation in a

cost-sensitive market like lubes ultimately comes down to either doing better at the same cost or doing the same for cheaper. Many of the biobased base stocks are excellent in performance, but the value (performance relative to cost) is lacking. Innovation to make biobased lubricants and greases feasible on the large scale must be a matter of enhancing value rather than maximizing performance whatever the cost."

> 'Understanding and leveraging natural mechanisms of human joints could lead to significant advances in the lubricant industry.'

Recommendation for lubricant marketers

"Lubricant formulators are often innovative with a keen interest in exploring new additive technologies," says Greaves. "When it comes to developing lubricant solutions that incorporate biobased additives, strong collaboration with suppliers is essential. Both companies must clearly understand the business case for pursuing such developments. Suppliers of biobased additives typically face significant development costs, which can be compounded by the even higher costs of commercialization, especially when global inventory registration is required. By providing comparative performance data across different technologies, suppliers can inspire confidence in formulators, encouraging them to undertake potentially costly development programs. Feedback from formulators also is crucial in this collaborative process."

Willett says that biobased additive suppliers need to add value and guidance to the process: "Clarify goals with the customer for biobased content, biodegradability and economics early into the development projects. Does it need to meet a subjective 'ecofriendly' claim (and what does that really mean to them and their end-users?), or should it meet USDA BioPreferred, European Ecolabel, Vessel General Permit (VGP), OSPAR/CEFAS or any number of other certifications? What is possible within the list of whitelisted components, biodegradability/biobased requirements and necessary performance testing might not easily carry over since each program has different objectives."

He gives an explanation: "Achieving biobased success can be a difficult process for many companies who may have built a solid foundation of expertise on petroleum over decades or even over a hundred years. These companies will have invested significant money into testing, field trials and approvals on their legacy products. Biobased formulations will have challenges and unique rules of thumb for selection and use due to their difference in oxidative stability, seal swell, lubricity, viscosity index and more. Change at large formulators and at their end-users will come in stages. Rather than jumping to a 100% biobased product with different rules and field behavior than what the formulator is experienced with, try hybrid of conventional and new biobased technology. European Ecolabel sets a 25% by weight target to claim 'biobased,' which is a good steppingstone to start making any difference sooner. This modest usage may even yield some performance benefits without straying too far from the blender's comfort zone. Success will ultimately rely on collaboration between suppliers and formulators with both sides continuing to learn more as the needs for biobased lubes continues to grow."

Beaver shares: "For lubricant developers who are interested in exploring the use of biobased additives in their formulations, understand the customers' (and potential customers') needs very well before commencing a formula development program, just as one would when using more conventional additives." He suggests: "Take steps to understand all the standards to be met, performance requirements and regulatory hurdles to be overcome to ensure a high-performance, sustainable solution that meets customers' needs. Work closely with your suppliers to understand the strengths and weaknesses of the additive technologies to avoid later pitfalls during development, lab testing and field trials. This is critical for the newer biobased additives whose characteristics and stability may be less well characterized or understood (even by their manufacturer) when compared to conventional additive systems. Don't overlook the valuable role that associations such as STLE play in educating suppliers, formulators and end-users."

Summary

Indeed, environmental conservation efforts are gaining importance in our societies. We should keep in mind that the environment is continuously contaminated with various kinds of pollutants, and any slight reduction is gladly acceptable. A large number of petroleum-based lubricants pollute the environment during or after use, mostly from spills and industrial processes. Various countries are restricting the use of petroleum-based lubricants in applications where lubricants can contact soil and water.[2] Ultimately, biobased and sustainable additives have a key role in shaping the future of lubrication technology, and the lubricant industry is encouraged to further explore and adopt these solutions.

Beaver rightly says: "As regulations become more stringent and limits to the use of conventional additives become more prevalent or more restrictive, the role of biobased additives can only increase." Beaver sees the move to more biobased additives and more truly sustainable lubricants as inevitable. The only real question is, he says: "How quickly can we as formulators work with the additive suppliers to provide viable biobased solutions that perform well at a competitive cost and use rate in our formulae?" More sustainable lubricants are the future, and the additives play a dramatic role in making the new sustainable products viable in the marketplace.

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