Biodegradable lubricants: Working definitions, review of key applications and prospects for growth

Multiple definitions for biodegradability have to be taken into consideration.

By Dr. Neil Canter
Contributing Editor

KEY CONCEPTS

The primary test procedure used to define the biodegradability of a specific substance is OECD 301.

The one global regulation that defines an environmentally acceptable lubricant is VGP.

The performance improvements seen with biodegradable lubricants are directly attributed to the availability of better base stocks.

An area of need is the development of additives that exhibit low aquatic toxicity and low bioaccumulation.

Terms such as "environmentally acceptable" have been used to categorize biodegradability. This has led to confusion in defining the concept of biodegradability. With the growing use of environmentally friendly lubricants and the increasing awareness of sustainability, as discussed in the STLE 2020 Report on Emerging Issues and Trends in Tribology and Lubrication Engineering,[1] there is need for providing some clarification about how to determine if a specific lubricant is, in fact, biodegradable.

The purpose of this article is to review the approaches used to characterize biodegradability and to identify the key lubricant applications that will require the use of environmentally friendly lubricants now and in the future.

Key industry experts were contacted to gain their insight on biodegradability and on lubricant applications where biodegradability will be important.

The following experts were interviewed.

1. Kevin Duncan, Croda Europe Ltd.
2. Leanne Heads, Croda Europe Ltd.
3. Nick Weldon, Croda Europe Ltd.
4. Dr. Martin Greaves, Dow Chemical
5. Dan Vargo, Functional Products
6. Dr. Erik Willett, Functional Products
7. Dr. Paula Vettel, Novvi LLC
8. Dr. Larry Beaver, RSC Bio Solutions
9. Darren Lesinski, Total Specialties USA
10. Dr. Girma Biresaw, United States Department of Agriculture (USDA)
11. Tyler Housel, Zschimmer & Schwarz

Working definitions for biodegradability

STLE member Dr. Larry Beaver, vice president, research & development, for RSC Bio Solutions in Indian Trial, N.C., claims that the most common working definitions for biodegradability are codified in the OECD 301A-F test methods.[2] He adds, "The most commonly referenced requirements are those for the U.S. EPA Vessel General Permit (VGP) 2013 (soon to be known as the Vessel Incidental Discharge Act, VIDA),[3] the Lubricant Substances Classification (LuSC) list[4] and the EU Ecolabel."

The Organization for Economic Co-operation and Development (OECD) defines biodegradability through three basic definitions that cover readily biodegradable, ultimate biodegradation and inherently biodegradable.

- **Readily biodegradable.** An arbitrary classification of chemicals that have passed certain specified screening tests for ultimate biodegradability. These tests are so stringent that it is assumed that such compounds will rapidly and completely biodegrade in aquatic environments under aerobic conditions. A substance is readily biodegradable if there is 70% removal of dissolved oxygen carbon and 60% of theoretical oxygen demand or theoretical carbon dioxide production obtained from respirometry test methods.[2]
- **Ultimate biodegradation (aerobic).** The level of degradation achieved when the test compound is totally utilized by microorganisms resulting in the production of carbon dioxide, water, mineral salts and new microbial cellular constituents (biomass). Ultimate biodegradation is reported as a specific percentage and is not defined by a particular value or range of values.[2]
- **Inherently biodegradable.** A classification of chemicals for which there is unequivocal evidence of biodegradation (primary or ultimate) in any test of biodegradability. A substance shows inherent, primary biodegradation if it exhibits biodegradation above 20% of theoretical. A substance shows inherent, ultimate biodegradation if it displays biodegradation above 70% of theoretical.[5]

Readily biodegradable, ultimate biodegradation and inherently biodegradable are three definitions for biodegradability according to OECD.

Leanne Heads, Global Product Safety and Regulatory Affairs manager for Croda Europe Ltd. in Snaith, UK, states that the European Ecolabel for Lubricants is used as a guide for defining biodegradability. She says, "EU Ecolabel[6] for lubricants allows for the use of freshwater (for example, OECD 301B) and marine methods (OECD 306) in determining biodegradability. Under the EU Ecolabel for lubricants and other relevant regulatory regimes, the substances within the lubricant are characterized for biodegradation potential, not the finished lubricant."

Heads indicates that there are two main definitions for biodegradability that are employed under the European Ecolabel for lubricants criteria. She says, "A substance is considered to be readily (aerobically) biodegradable in the environment if 70% degradation is achieved based on testing of dissolved organic carbon or if 60% of the theoretical maximum is obtained for oxygen depletion or carbon dioxide depletion."

Both tests are run for 28 days.

Two other criteria that will indicate a substance is readily biodegradable, according to European Ecolabel criteria, are if the ratio of biological oxygen demand to chemical oxygen demand is ≥0.5 and/or if other scientific evidence is available to demonstrate that the lubricant can be degraded (biotically and/or abiotically) in the aquatic environment to a level >70% within a 28-day period.

The second definition is for inherently (aerobically) biodegradable. Heads says, "Two criteria for inherently biodegradable are the substance achieves a 70% result after 28 days in an appropriate test or if

The lubricants industry uses standard test methods such as OECD 301B to classify substances as inherently, ultimately or readily biodegradable.

the substance produces greater than a 20% but less than 60% result in tests based on oxygen depletion or carbon dioxide generation."

STLE member Dr. Erik Willett, vice president of technology and development for Functional Products in Macedonia, Ohio, provides his perspective on the definition of biodegradability. He says, "Biodegradability is generally understood to be >60% degradation by the CEC L-33-T-82 or OECD 301 test methods. OECD 301 is the most prominent test these days, but there is far more extensive data available from the CEC L-33 test in the literature. Both of these 28-day methods quantify biodegradability by measuring different parts of the process. The CEC test can typically give 10-20 points higher than the OECD procedure, i.e., an ester might be 100% degraded, according to CEC, but 80% by OECD."

There is need for providing some clarification about how to determine if a specific lubricant is, in fact, biodegradable.

Willett revealed that most formulators either want to just meet the readily biodegradable status plus a margin of error (60%-70%) or strive for >99% with few cases in between. He admits, "Very few customers are interested in making inherently biodegradable (20%-60%) lubricants but products designed to meet certifications like USDA BioPreferred, which focus on % biobased content and might fall into this category by consequence."

STLE member Dr. Paula Vettel, technical director, formulations and regulatory for Novvi LLC in Emeryville, Calif., indicates that the OECD established method 301 in 1992 to standardize biodegradability definitions and testing. She says, "OECD 301 provides methods for biodegradation testing of chemicals in general. OECD 301B and OECD 301F are the preferred methods for poorly soluble materials such as lubricants. OECD 302 can be used to measure inherent biodegradability."

Vettel classifies each biodegradability category by the degree of biodegradation over a 28-day time frame.

- Readily biodegradable ≥60% in 28 days and within 10 days (10-day window)
- Ultimately biodegradable ≥60% in 28 days, no 10-day window
- Inherently biodegradable >20 to <60% in 28 days or longer
- Non-biodegradable ≤20% in 28 days.

STLE member Darren Lesinski, technical director, automotive, industry & U.S. IOEM for Total Specialties USA in Linden, N.J., indicates that four definitions for biodegradability are in use.

- Primary biodegradation is defined as a minimal modification of a substance by a microorganism that causes a change in some measurable property of the substance.
- Ultimate biodegradation is the degradation achieved when a substance is totally utilized by microorganisms, resulting in the production of carbon dioxide, methane, water, mineral salts and new microbial cellular constituents. This term usually refers to vegetable oil-based products.
- Readily biodegradable—Using ASTM D5864 or OECD 301B, 60% or more of the test material carbon must be converted to carbon dioxide in 28 days. Usually this term is associated with glycol or ester-based lubricants whether synthesized from renewable resources (oleochemical) or synthetic esters (*class HEES, see Table 3 on Page 43*).
- Inherently biodegradable—This is a classification of chemicals for which there is unequivocal evidence of biodegradation (primary or ultimate) in any biodegradability test. Mineral oil-based products are usually associated with inherent biodegradability due to their low degree of biodegradation in ASTM D5864 or OECD 301B (typically less than 40%). Products that are classified as inherently biodegradable also are pollutants and, if disposed of in the environment, are subject to fines, clean-up regulations and long-term remediation.

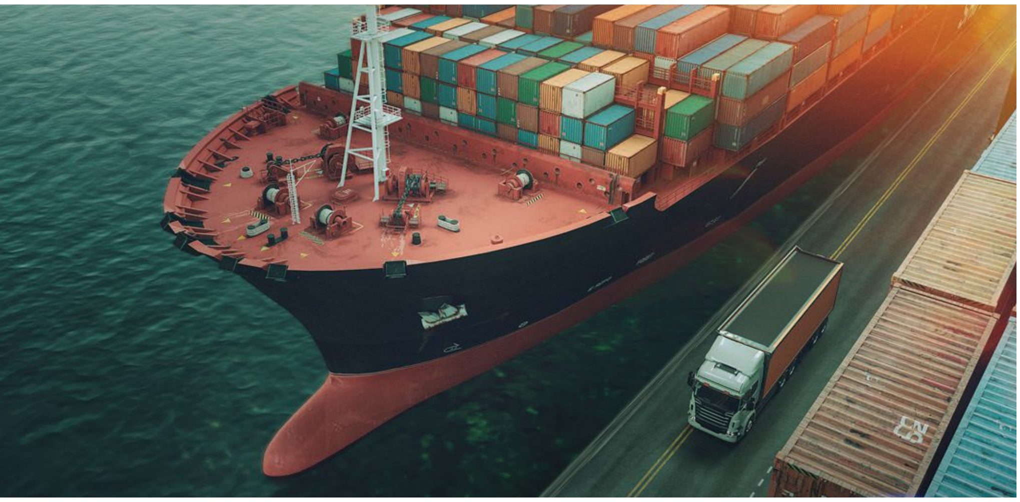
Lesinski says, "We believe that 'readily biodegradable' is the most important as it pertains to application and process. However, we must consider 'renewable' when talking about biodegradable lubricants."

STLE member Tyler Housel, director of sales – Lexolube for Zschimmer & Schwarz in Milledgeville, Ga., says, "Biodegradability is a measure of whether bacteria or other natural organisms can break down a substance into harmless products when released into the environment. Given enough time and the right conditions, most carbon-based substances will break down. The lubricants industry uses standard test methods such as OECD 301B to classify substances as inherently, ultimately or readily biodegradable."

Housel also points out that biodegradability can be related to concepts such as biobased, renewable, sustainable and eco-friendly, but he maintains that these terms do not necessarily have the same meaning.

STLE member Dan Vargo, senior research chemist for Functional Products, says that one needs to look at toxicity and renewability in addition to biodegradability. He says, "For toxicity, lubricants that are considered to be non-toxic to the environment or environmentally friendly can be measured by OECD 201-203 tests for ▶

▶ acute toxicity, OECD 210-211 or ASTM D6064 for chronic toxicity. For renewability, lubricants with biobased carbon contents in excess of 25% (in line with CEN 16227) are considered to be renewable as measured by ASTM D6866."



The EPA published the VGP setting out standards for the use of environmentally acceptable lubricants in all oil-to-sea interfaces where marine vessels enter U.S. waters. The impact of this regulation has been worldwide due to the global aspects of maritime trade.

Global regulations

Nick Weldon, technical marketing manager for Croda Europe Ltd., says, "For specific global regulations, only one piece of major governmental legislation has been enacted, which is the VGP. To be approved for use, the lubricant in question must conform to specific labelling standards, including European Ecolabel, Blue Angel, Swedish standard SS 155434 and 155470 or OSPAR."[7]

Vettel provides further details on the guidelines for the U.S. VGP regulation and on OSPAR. She says, "VGP was enacted in 2013 and is part of the Clean Water Act. This act covers all vessels that are over 24 meters and used most of the Ecolabel criteria in the definitions used for environmentally acceptable lubricants. The VIDA was expected in late 2018 but will wait until the EPA publishes National Standards of Performance (NSPs) and the U.S. Coast Guard develops implementation regulations for the NSPs. The timing for VIDA is not expected for four years."

Fifteen countries located in Europe that surround the North Atlantic Ocean established the OSPAR Commission in 1992 to control and prevent chemical pollution from ships and offshore equipment. Vettel says, "They have a very stringent set of criteria, which, if met, allows a lubricant or components to be placed on their approved list."

STLE member Dr. Martin Greaves, research leader at The Dow Chemical Co. in Horgen, Switzerland, indicates that the two regions spurring innovation in the area of biodegradable lubricants are Europe and the U.S. He says, "In Europe, The EU Ecolabel criteria for lubricants sets out a comprehensive list of requirements with the aim of promoting products with limited impact on the environment. Lubricants are segmented into three categories that include Total Loss Lubricants (TLL), Partial Loss Lubricants (PLL) and Accidental Loss Lubricants (ALL), each having its own requirements to meet the Ecolabel standards. Lubricants that qualify under the EU Ecolabel also should conform with minimum technical performance requirements such as the ISO 15380 technical requirements for a hydraulic fluid."

Greaves considers EPA's publication of the VGP to be a significant development in the U.S. for biodegradable lubricants. He says, "The EPA published the VGP setting out standards for the use of environmentally acceptable lubricants in all oil-to-sea interfaces where marine vessels enter U.S. waters. The impact of this regulation has been worldwide due to the global aspects of maritime trade. This has stimulated a significant amount of innovation in new technology solutions for using biolubricants. Lubricants derived from vegetable oils, synthetic esters, polyalkylene glycols (PAGs) and polyolefins have found acceptance."

Housel focuses on the use of the OECD 301B biodegradation test, which he indicates is used most often because lubricants under evaluation are primarily water insoluble materials. He says, "Unfortunately, OECD 301B can have poor repeatability because bacterial populations can vary by geography or season and evolve in their natural environment. Further complicating test results is that bacteria can only digest substances that are available in the aqueous partition where they live and might struggle with high viscosity insoluble materials that do not disperse well. The results also are affected by the physical form of the test substance."

Housel cites the following four general rules to predict whether a substance is biodegradable. He notes that for a specific substance, any one of these rules might dominate.

1. Vegetable oils (triglyceride esters) and synthetic esters are more biodegradable than pure hydrocarbons.
2. High viscosity/high molecular weight slows biodegradability.
3. More polar groups improve dispersibility.
4. Branched hydrocarbon chains reduce biodegradability.

Heads provides examples of lubricant types that can be classified as TLL, PLL and ALL under the Ecolabel guidelines. She says, "TLLs include chainsaw oils, wire rope lubricants and concrete release

	Cumulative mass percentage (%w/w) limits for substances present in the product			
	ALL	PLL	TLL	Greases (ALL, PLL, TLL)
Readily aerobically biodegradable	> 90	> 75	> 95	> 80
Inherently aerobically biodegradable	≤ 10	≤ 25	≤ 5	≤ 20
Non-biodegradable and non-bioaccumulative	≤ 5	≤ 20	≤ 5	≤ 15
Non-biodegradable and bioaccumulative	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1

Table 1. **Cumulative mass percentages for substances in each of the three EU Ecolabel criteria, with respect to their biodegradability and bioaccumulation potential, are shown. Grease are covered in a fourth category.** *Table courtesy of Croda Europe Ltd.*

agents. Gear oils intended for the use in open gears, stern tube oils and two-stroke oils are potential PLLs. Hydraulic fluids, metalworking fluids and closed gear oils are all examples of ALLs. Greases can be classified in all three of these categories."

Table 1 lists the cumulative mass percentage (% weight by weight, w/w) for substances in each of the three EU Ecolabel criteria with respect to their biodegradability and bio-accumulation potential. Greases are covered in a fourth category.

Lesinski discussed work done by CEN, Technical Committee TC 19 that is responsible for "Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin." He says, "This committee prepared a new European standard DIN EN 16807 entitled, "Criteria and requirements of bio-lubricants and bio-based lubricants" that was approved in May 2016 and published in December 2016. The standard finally qualifies the term "biobased product" with respect to tests on the fully formulated lubricant. It furnishes minimum requirements for all kinds of biolubricants and biobased lubricants. Two analytical standards (ASTM D6866 and EN 16640) are recommended for use in determining biobased carbon content measurements."

Lesinski states that the EU Ecolabel has specified a minimum biobased carbon content of 25% for lubricants using the terms "biobased" or "biolubricant."

Several of contributors pointed out that there is no single regulation that defines a biodegradable lubricant. Beaver says, "The closest we have is a definition of an environmentally acceptable lubricant as codified in the U.S. EPA VGP."

Lesinski adds, "If a universal test method can be developed and accepted by all, then that will play a key role in defining biodegradable lubricants. Other factors that must be considered for this method to be accepted are reduction of carbon dioxide and the use of renewables."

Vettel provides some hope for standardization when discussing the revision of the Ecolabel in 2018. She says, "Global regulations do contain important definitions of biodegradability that are reasonably consistent, except not all make the distinction between readily and ultimately biodegradable. The revision of the Ecolabel involved a working group with representatives both from the lubricant industry and environmental regulations. Valuable information was shared, and the regulators gained an understanding of the constraints they were proposing to formulators. A positive outcome from this meeting was a loosening of the requirement to meet the 10-day window."

Evolution of biodegradable lubricants

Beaver says, "The greatest impact in accelerating the growth of biodegradable lubricants has been the development of high-performance synthetic hydrocarbon base oils. This technology is both readily biodegradable and more oxidatively and hydrolytically stable than the ester technology that was used in the past."

Beaver continues, "It is now possible to create biodegradable lubricants that outperform many of the non-biodegradable lubricants. It also is possible to use synthetic and biosynthetic hydrocarbon base oils to create environmentally acceptable lubricants that are more stable than both non-biodegradable and previous biodegradable technologies."

Willett believes that biodegradable lubricants have moved from the old notion of 'good for the environment, poor for performance.' He says, "Synthetic biodegradable lubricants are now seen as quite high in performance. Certain polyalphaolefins (PAOs), PAGs and polyol/complex esters are exciting and robust base stocks. And our industry's understanding of vegetable oils and their specific needs has grown substantially in the past 20 years."

The two regions spurring innovation in the area of biodegradable lubricants are Europe and the U.S.

In evaluating the performance of biodegradable versus non-biodegradable lubricants, the most common metric that Willett uses is the RPVOT oxidation test (ASTM D2272). He says, "Natural vegetable oils are limited to 50-200 minutes, PAGs (some biodegradable) up to 400 minutes, synthetic esters from 800-1,500 minutes and PAOs in the several thousand minutes."

Table 2 lists RPVOT figures for representative examples from these base stock classes.

Housel feels that the performance of biodegradable lubricants has improved

Category	Biodegradable?	Example (w/ 0.5% Antioxidant)	D2722 RPVOT, minutes
Vegetable Oils	Yes	Vegetable and High Oleic Veg with no AO	< 10
	Yes	Soybean, Canola, High Oleic Canola	50
	Yes	High Oleic Soy	120
	Yes	High Oleic Sunflower	150
PAG	Yes for Low Visc	Water Soluble PAG	40
	Yes for Low Visc	Oil Soluble PAG	400
Synthetic Ester	Yes	Adipate	800
	Yes	Polyol Ester	1,000
	Yes	Estolide	1,500
Mineral Oils	No, possibly 20-40%	Group I/II and White Oil	100 - 500
Group III	Yes for Low Visc	4 cSt Group III	800
PAO	Yes for Low Visc	mPAO	1,500 - 3,000

Table 2. **RPVOT oxidation test figures (ASTM D2272) for various base stocks are shown.** *Table courtesy of Functional Products.*

Lubricant Samples Tested 200°C for 20 Hours	Ultra-High Temperature Food Grade Lubricant	Biodegradable High-Temperature Food-Grade Lubricant	Competitive Standard
Viscosity	ISO 46	ISO 46	ISO 46
Max Use Temperature	250°C	220°C	Below 200°C
Biodegradability	No (inherent)	Readily	No (inherent)
% Evaporation	1.2%	3.4%	7.4%
% Liquid	92.9	90.4	0

Figure 1. **The improved performance of biodegradable lubricants can be shown in test results for three ISO 46 lubricants evaluated for use as chain oils. Thermal stability testing shows that the biodegradable, food-grade lubricant (*middle column*) displays comparable performance to an incumbent food-grade lubricant (*left column*) and a non-biodegradable, petroleum-based industry standard (*right column*).** *Figure courtesy of Zschimmer & Schwarz.*

over the past decade. He says, "More base oils have passed OECD 301B, so today's formulator has a wide palette of readily biodegradable ingredients. Several biodegradable fluids have been developed that offer excellent oxidative and thermal stability, lubricity and meet or exceed the performance requirements of traditional lubricants in most applications. One example that relates to our business is the recent availability of odd carbon chain carboxylic acids. These are used to make biodegradable polyol esters that can be used over a wider temperature range."

Housel is optimistic that the currently available biodegradable lubricants can meet any potential application at present. He says, "In situations where biodegradability is a must-have characteristic, biodegradable lubricants exist that can do the job."

An example of the improvement in the performance of biodegradable lubricants is illustrated for food-grade lubricants (meeting H1 requirements) in Figure 1. In this example, three ISO 46 lubricants were heated to 200 C for 20 hours to assess their thermal stability for use as chain oils.

The readily biodegradable, food-grade lubricant (*middle column of Figure 1*) exhibited a maximum evaporation of only 3.4% while remaining liquid during the procedure. An incumbent, food-grade lubricant (*left column*) exhibited slightly better thermal stability but is not biodegradable. The third sample is a non-biodegradable, petroleum-based industry standard (*right column*), which showed inferior thermal stability, a higher degree of evaporation, and turned completely solid.

Greaves feels that historically biolubricants often had a poor image due to their lack of performance in equipment. He says, "But inclusion of technical performance standards in the new environmental schemes has raised the performance of environmentally acceptable lubricants to new levels. Over the past 15 years, a stronger alignment has occurred for meeting technical performance requirements in equipment. The Ecolabel stipulates the need of lubricants to conform with minimum technical performance requirements. For example, bio-hydraulic fluids ▶

should meet the ISO 15380 requirements for a hydraulic fluid and bio-gear oils (closed gears) should fulfill the specification set out in ISO 12925-1.

Lesinski says, “An illustration of a class of hydraulic fluids that are biodegradable, yet meet specific OEM specifications, is shown below. This category of hydraulic fluids is formulated with a synthetic base stock, is water soluble and meets requirements for use in VGP applications.”

Benefits include:

- Readily biodegradable—>70% per OECD 301F
- Excellent antiwear, anticorrosion and antifoam properties
- Excellent shear stability and thermal stability
- No sheen, passes U.S. EPA CFR 435 Static Sheen Test
- Very high viscosity index
- Excellent low-temperature properties
- Meets major OEM specifications.

Kevin Duncan, marketing application specialist for Croda Europe Ltd., is optimistic about the growth of biodegradable lubricants. He says, “The number of products that are offered have increased dramatically over the last decade, and long gone are the days where a lubricant producer would have a token ISO 46 hydraulic fluid in the product line. Formulators have realized that with the right combination of synthetic base stocks and enhanced additive packages, environmentally acceptable lubricants can outperform traditional mineral oil lubricants in most areas. The limiting factor is more of initial cost than overall cost benefit.”

Duncan feels that the improved performance of biodegradable lubricants can be attributed to the growing use of new, synthetic base stocks in applications such as marine stern tube oil applications that conform to VGP. He says, “The use of specialty synthetic base stocks can minimize the effects associated with the first generation of biodegradable lubricants based on simple triglycerides, animal fats or seed oils. Triglycerides or the polyol ester, trimethylolpropane (TMP) trioleate, can hydrolyze, but specialty synthetic esters will not.”

Figure 2 shows the hydrolytic stability of the most common synthetic base stocks used. Each category of base stock is designated by the ISO classifications shown in Table 3.

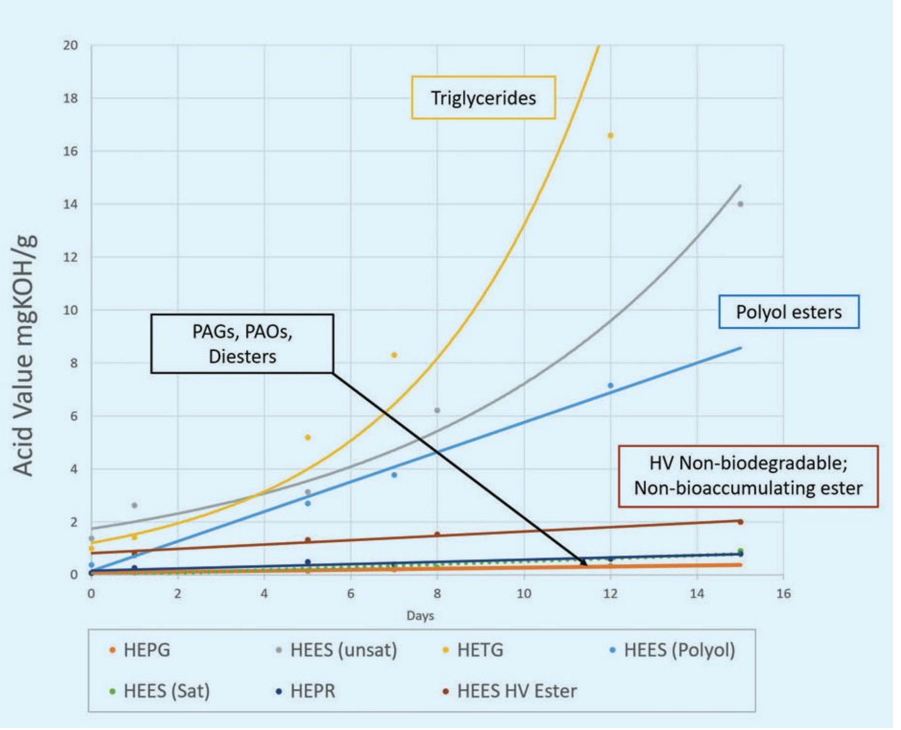


Figure 2. **Hydrolytic stabilities for synthetic base stocks are shown.** *Figure courtesy of Croda Europe Ltd.*

Vettel also agrees that the performance of biodegradable lubricants has improved tremendously over the last decade. She says, “Biodegradable lubricants have a bad reputation when low-cost vegetable oils were the main constituent. However, new technology based on synthetic hydrocarbons allows the user to maintain the high performance found with mineral oils while getting the additional benefit of biodegradability and low toxicity.”

Vettel adds, “There are new biodegradable hydrocarbon lubricants available that combine the high technical performance of traditional mineral oils with the improved environmental features of biodegradability, low toxicity and sustainability that were the hallmark of vegetable oils.”

Growth of biodegradable lubricants

Most of the respondents indicated that marine lubricants are the one application where growth of biodegradable lubricants is accelerating. This prospect is due to a large extent to the implementation of VGP.

Vargo says, “VGP and marine applications already mandate environmentally acceptable lubricant status through one of several programs. With climate change and the possibility of rising tides or more severe weather, there will be a need for expanded use of marine lubricants for everyday life or in emergency response. There is significant growth in recreational and water sports activities over the last few years. Some activities include fishing, boat racing and sailing. Investment by the government into the naval ship fleet also will accelerate the growth of biodegradable lubricants.”

Weldon indicates that the reason marine has become a pivotal application is the increase in shipping goods and concern about pollution. He says, “A conservative estimate suggests that long-term shipping is expected to rise from 182 million, 20-foot equivalent units (TEUs) to 464 million TEUs by 2066. Pollution output from marine shipping is coming under increasing scrutiny, and we have already seen the effects of the IMO 2020 rules on sulfur in marine fuels.”

Lesinski points out that any application that is near a waterway or a storm/drainage system is a significant growth opportunity for biodegradable lubricants. He says, “Examples include flood gates and damning hydraulics systems.”

Greaves indicates that electric vehicles might represent a growth opportunity for biodegradable lubricants. He says, “Recent developments in multipurpose lubricants/coolants for electric vehicles demonstrate the utility of biodegradable fluids in an application where environmental protection should be encouraged. This application has the potential to reshape the global lubricants market."

Willett believes that reducing the cost of biodegradability testing is an important consideration in the growth of biodegradable lubricants. He says, "Just the minimum performance requirements for an Ecolabel hydraulic fluid (ISO 15380 HETG) will cost $10,000-$15,000 if testing is successful in a single round. Additional biodegradability testing adds several thousand dollars. Lower cost biodegradation testing would lower a huge barrier for numerous small blenders to enter the market with reliable biodegradation data. More accessible testing also would allow formulators to pioneer new approaches and facilitate innovation in high-performance biodegradable lubricants."

A second challenge for biodegradable lubricant manufacturers is to figure out a better strategy for developing high viscosity products. Willett says, "It is very difficult to achieve a readily biodegradable formula above ISO 1000. Many biodegradable formulations over ISO 680 are inelegant mixtures of many different chemistries, which might age poorly together in the field. If better high viscosity options become available, then you could expect more penetration of biodegradable lubricants into the mining and heavy gear open lubricants markets."

Beaver feels that for biodegradable lubricants to grow in land-based applications, new regulations are required. He says, "These regulations should be designed to minimize the impact of spills and decrease operator costs due to costly clean-ups."

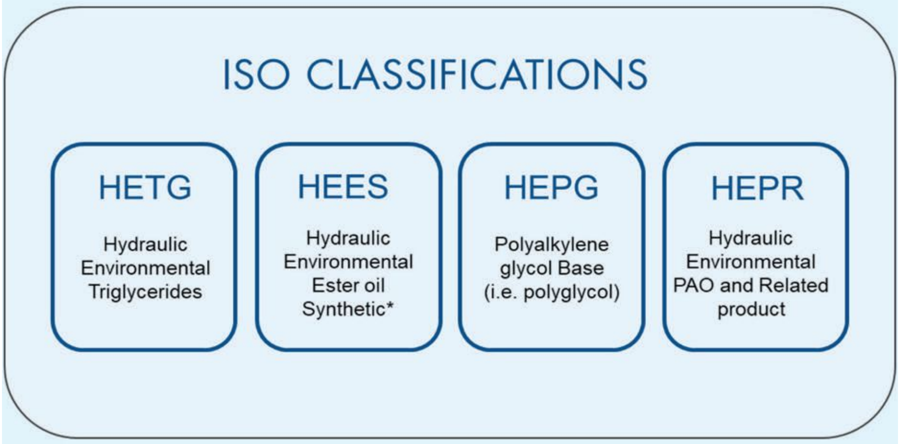
More synthetic lubricant base stocks options are leading to the conclusion that growth of this market segment will facilitate the wider use of biodegradable lubricants. Greaves comments, "Many synthetic lubricants are now marketed as biolubricants, and one factor influencing this is the design of synthetic lubricant base stocks from oleochemical feed stocks. Many synthetic esters are manufactured from oleochemical feed stocks and are biodegradable with a high renewable carbon content. Some types of PAGs are biodegradable and can be derived, in part, from oleochemical feed stocks. In recent years, the introduction of hydrocarbon base fluids from renewable feed stocks and the emergence of estolides has provided the industry a wider choice of developing biolubricants."

Duncan says, "From our standpoint, biodegradable and synthetic are one and the same thing. Natural seed oils have been broken down and then rebuilt as controlled molecules for a number of years. The result is that a wide range of synthetic lubricants are now available for biodegradable lubricant manufacturers."

Vettel says, "The term synthetic is more of a marketing term than a technical term. The need for lower viscosity fluids in engines, transmissions and other applications require high viscosity index, low bulk viscosity and low volatility base stocks. This trend will drive the use of biodegradable lubricants, which also are described as synthetic."

Housel feels that biodegradable and synthetic are two different concepts. He says, "The term 'synthetic' has no clear chemical definition in our industry, but most would agree vegetable oils are not synthetic. Yet, they are highly biodegradable."

Housel further examines the terminology used surrounding biobased fluids and comes to the conclusion that being biodegradable is not necessarily



* Most commonly used. Huge variation

HETG: Triglyceride Base (vegetable oils, i.e., plant oils)
A biodegradable hydraulic fluid which uses triglyceride esters as the base fluid. Vegetable oils are triglyceride esters.

HEES: Synthetic Ester Base (similar to triglyceride but with a non-vegetable-based acid & alcohol)
A biodegradable hydraulic fluid which uses synthetic esters as the base fluid. Synthetic esters share a similar chemical structure to HETG types, but are synthesized rather than derived from natural sources.

HEPG: Polyalkylene Glycol Base A biodegradable hydraulic fluid that uses polyalkylene glycols (PAGS) as the base fluid.
PAGS are synthesized from hydrocarbon oxides.

HEPR: Other Base Liquid – primarily polyalphaolefins
HEPR = Hydraulic Environmental PAO and Related products = A biodegradable hydraulic fluid which uses polyalphaolefins and related hydrocarbons as the base fluid. These base stocks are synthesized from crude oil derivatives.

Classification of environmentally acceptable hydraulic fluids from ISO 6743-4: 2015. Further descriptions adapted from white paper published by BioBlend. This is available here: ***www.bioblend.com/wp-content/uploads/2019/12/Hydraulic-Fluid-Classifications.pdf.***

Table 3. **ISO classifications for base stocks used in environmentally acceptable hydraulic fluids are shown that conform to ISO 6743-4:2015.** *Table courtesy of Croda Europe Ltd.*

Figure 3. **Dialkyl phosphonates (r=alkyl) are synthetized by using a hydrophosphonation reaction that utilized methyl linoleate.** *Figure courtesy of USDA.*

synonymous with being environmentally friendly. He says, "It is important to note that biodegradable fluids are not always considered environmentally friendly. The USDA BioPreferred program requires ingredients that are primarily biobased (with limits on petroleum allowed). In contrast, the Ecolabel allows petroleum-based ingredients but does not allow bioderived ingredients unless they are grown 'sustainably.' This leads to confusion that can best be sorted out by determining the regulations or specifications that apply to each application before deciding what ingredients to use."

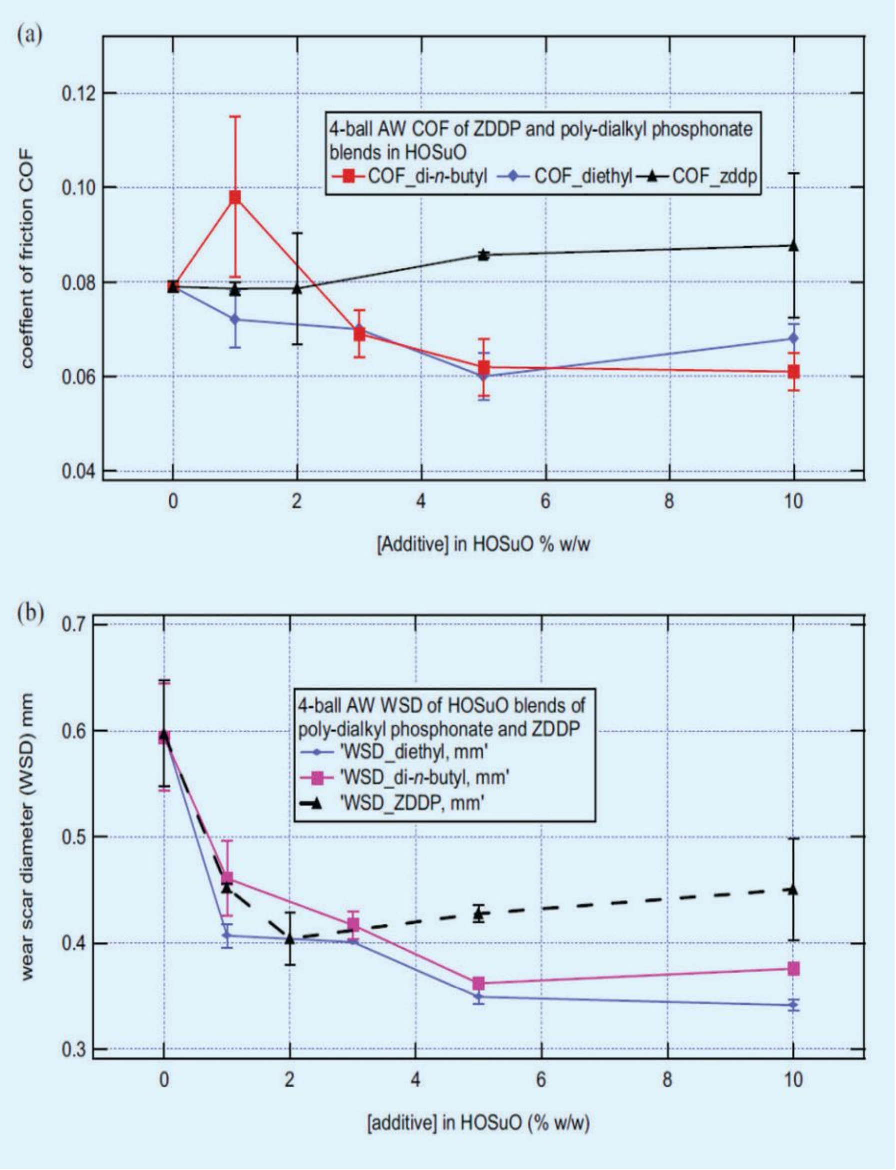


Figure 4. **Four-ball antiwear testing of the phosphonates compared to ZDDP was conducted in high oleic sunflower oil (HOSuO) and showed equal or better antifriction and antiwear properties.** *Figure courtesy of USDA.*

Additives

The late STLE member Dr. Girma Biresaw, research chemist/lead scientist in the Bio-Oils Research Unit at the USDA in Peoria, Ill., considered the additive portion of lubricant formulations to be rather complex, making it difficult for the formulator to work with biodegradable components. He said, "Additives are used to perform specific functions (e.g., antifriction, antiwear, biocide, defoamer, etc.) in a lubricant formulation. Some additives such as friction modifiers are biodegradable, but a vast majority are not, and formulators have no choice but to use petroleum-based, non-biodegradable additives in their work."

One example Biresaw cited is the development of biobased antiwear additives. He said, "Currently, there are no viable biobased antiwear additives in the market. As a result, formulators are forced to rely on zinc dialkyldithiophosphates (ZDDPs) and other petroleum-based, antiwear additives for their biobased formulations."

A new biobased pathway, utilizing methyl linoleates derived from soybean oil, was used to synthesize dimethyl, diethyl and di-n-butyl phosphonates.[8] These additives were prepared through a hydrophosphonation of the two double bonds in methyl linoleate, as shown in Figure 3.

Evaluation testing was conducted by adding the phosphonates at various treat rates (from 0% to 10%), to high oleic sunflower oil and running antiwear friction tests and wear tests using a four-ball tribometer. In the study shown in Figures 4(a) and 4(b), a ZDDP-based formulation was used for comparison purposes.

Biresaw concluded, "The results show that these biobased dialkyl phosphonates exhibit equal or better antifriction and antiwear properties compared to ZDDP. This work shows they have the potential to replace ZDDPs and other petroleum-based antiwear additives currently used in the market."

Identifying antioxidants and copper passivators without aquatic toxicity would be big drivers in advancing cost-effective biodegradable lubricants with lower aquatic toxicities, without the need for synthetic base stocks.

Housel claims that additives are important in affecting lubricant performance but have little impact on biodegradability of the overall formulation. Synthetic esters can be used as additives to improve lubricant performance. He says, "Properties such as lubricity, seal swell and additive solubility can be improved through using biodegradable synthetic esters up to a concentration of 10%. But the impact on biodegradability is small unless the primary base fluid is biodegradable."

With the challenge of developing high viscosity biodegradable lubricants, Housel sees esters as a potential option. He says, "Vegetable oils, a base stock used in biodegradable lubricants, are only available in a narrow viscosity range around ISO 32. High viscosity, biodegradable complex esters are additives that allow a producer to expand the viscosity range and maintain biodegradability."

Greaves points out that natural and synthetic esters used in formulating biolubricants are vulnerable to hydrolytic stability in environments where ingress of water into the lubricant is possible. He says, "To forestall the shortening of lubricant life, additive technologies have emerged that can retard the rate of hydrolysis. For example, carbodiimides can act as acid scavengers, and specific types of PAGs can perform as water absorbers, the latter also being biodegradable."

Environmentally acceptable lubricants can outperform traditional mineral oil lubricants in most areas.

Greaves predicts that demand for water-based lubricants such as for gear oils will emerge and lead to opportunities for better formulated biodegradable lubricants. He says, "This trend is aligned with the movement toward using lubricants that positively contribute to sustainability improvements and a circular economy. The challenge with using water-based lubricants remains in meeting equipment performance specifications, and this challenge is a fertile area for more innovation in the future."

One of the weaknesses of vegetable oil lubricants has been their lack of oxidative stability. Willett says, "Where a treat rate of 0.25-0.5 wt.% antioxidant might be sufficient in mineral oil-based lubricants, formulators really need 1.5-2.0 wt.% antioxidant in a high oleic vegetable oil to achieve even a modest 120-150-minute RPVOT. However, the two most widely used antioxidant chemistries, diphenyl amines and hindered phenolic derivatives, carry aquatic toxicity hazards. Other antioxidants have similar complications. Phosphites have their own aquatic toxicities, and phosphorus is unwanted in water run-off. Sulfur based, methylene bis dithiocarbamates are promising but copper corrosion from elevated usage will require a slight amount of aromatic triazoles, which also have aquatic hazards."

Willett states that identifying antioxidants and copper passivators without aquatic toxicity would be big drivers in advancing cost-effective biodegradable lubricants with lower aquatic toxicities, without the need for synthetic base stocks.

Beaver considers the correct choice of additives to be the key to the performance of all lubricants including biodegradable lubricants. He says, "Additives can influence the biodegradability of a finished lubricant. There is a fine line to walk when balancing biodegradability of a lubricant with its ultimate stability in service. Some additives that improve oxidative stability have been shown to decrease biodegradability in the OECD 301 series of biodegradation tests."

Beaver calls for more work to be done in developing biodegradable lubricant additives. He says, "This is an area of need for this industry. While the LuSC list contains many approved additives, the number of new additives that offer low aquatic toxicity and low bioaccumulation in fully formulated products is limited. We have seen improvements in viscosity modifier technologies, but there is more work to be done to improve the stability of these systems."

Vettel believes that today's additives do not affect the biodegradability of a lubricant, unless non-biodegradable thickeners are used in significant amounts. She says, "Future additives can be made with biodegradable and/or sustainable base stocks, or the 'backbone' of some additives can be made with sustainable and/or biodegradable components that can be used to lower their impact on the environment. This is a longer-term idea that needs consideration and should involve the use of ashless additives to lower environmental toxicities."

Lesinski says, "Certain additives play a key role in the biodegradable performance of a lubricant. Selection and balance are keys to maximize that benefit. Additives that deter biological activity should be avoided or kept to a minimum if no other pathway can be utilized."

He indicates that the pandemic has stressed long supply chains that stretch between continents and says, "Localization and dual sourcing are key virtues during the pandemic. Ports or entire countries were shut down for weeks, with little notice and left many stranded with long lead times. Sourcing of vegetable oils locally will prove to be more reliable than oil imports or even synthetic ester production. The latter might require the import/export of alcohols and acids produced outside of the local market."

The COVID-19 pandemic has stressed long supply chains that stretch between continents. Sourcing of vegetable oils locally will prove to be more reliable than oil imports or even synthetic ester production.

COVID-19

At the time this article was written, the COVID-19 pandemic has been adversely affecting the use of lubricants around the globe for nearly one year. The contributors were asked for their insight on how this health crisis will impact the use of biodegradable lubricants.

Weldon says, "The COVID-19 pandemic has forced governments to prioritize what they work on, what they spend their money on. The type of discussion and legislation needed to increase demand for biodegradable lubricants has been shelved and discussions on carbon dioxide targets delayed. For example, the COP26 United Nations Climate Change Conference has been moved from 2020 to 2021, which means that strong legislation that could greatly improve demand for environmentally acceptable lubricants will be delayed."

Weldon expresses hope that more awareness of the environment and combating climate change, especially in local government, policies and actions designed to combat pollution, might filter up to national governments and beyond.

Beaver notes that the pandemic has impacted users of biodegradable lubricants and the ability to get testing done. He says, "We have seen a substantial impact due to shutdowns, cancelled dry docks and decreased staffing at OEMs. The impact on international shipping has been dramatic. Productivity, internally and at external testing laboratories, has decreased due to short staffing."

The availability of better base stocks is leading to the growth of biodegradable lubricants, which are displaying performance equivalence to mineral oil-based lubricants in many applications. Regulations such as VGP also are promoting biodegradable lubricant use. Further growth will be dependent upon development of more biodegradable additives, improved cost performance and better environmental awareness in applications beyond those linked to the marine industry.

Note: This article on biodegradable lubricants is dedicated to the memory of Dr. Girma Biresaw of the USDA, who passed away as the article was being prepared. Girma had prepared his contribution to the article, and his colleagues at USDA asked me to include it. They assisted with the review, and I appreciate their support during this difficult time.

Girma was a passionate believer in biodegradable lubricants and spent his time doing research to promote their use and growth. He was a dedicated STLE volunteer who was the chair and a considerable contributor to the STLE Biofuels and Biolubricants Education Course given at the STLE Annual Meeting.

We will miss Girma's dedication to the growth of biodegradable lubricants and his tireless efforts to promote their use within STLE and in the lubricant industry.

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