Article Title: Fundamentals of Biobased and Biodegradable Lubricants; A Real World Perspective

Author: Mark Miller, CEO, Terresolve Technologies

Introduction

One has only to look around to see green initiatives. Bio-fuels, wind energy, renewable fibers are just a few of the environmental initiatives that have recently made headlines. Meanwhile, for the past several years, industry has been quietly looking into and utilizing environmentally safer, readily biodegradable and non-toxic fluids.
The benefits of environmental lubricants are well known. Their biodegradable properties allow them to break down in the environment reducing the negative impact from leaks and spills. They can be non-toxic, meaning they won't hurt operators, animals or plants that come in contact with the fluid. Furthermore, they are renewable and reduce dependence on foreign petroleum oil.

Conventional knowledge has focused on the limitations of vegetable oils as base stocks for lubricants. The weaknesses of the oxidative stability, the cold temperature performance and incompatibility with elastomers are well documented. Early generation biobased lubricant formulators utilized performance chemistry similar to those used in petroleum-based fluids, creating lubricant products that did not meet industrial performance requirements. Over the past decade, however, improvements in vegetable and other base stocks, improvements in performance chemistry, and improvements in formulation expertise have allowed the development of biodegradable products with performance similar to or better than conventional petroleum fluids.

One of the main reasons for concern about lubricant environmental safety is that a vast quantity of industrial lubricants find their way into the environment. In fact, the National Oceanic and Atmospheric Administration (NOAA) estimates over 700 million gallons of petroleum oil enter the environment each year, over half of which is through irresponsible and illegal disposal. Industry experts estimate that 70% to 80% of hydraulic fluids leave systems through leaks, spills, line breakage and fitting failure. Petroleum is persistent and toxic. It damages living organisms including plants, animals and marine life for many years. In addition, the Coast Guard, EPA and local governments are increasing the range of responsibility of lubricant releases including significant fines and cleanup costs.

In addition to regulatory pressure, industry is frequently faced with clients and stakeholders who are concerned with petroleum hydraulic fluids getting into the environment. Even a small amount of petroleum oil could contaminate an area and cause it to be classified as hazardous.

Release to the environment

As demands on lubricant systems increase, the likelihood of accidental release of fluids increases. Increased operating temperatures, pressures and working cycles shorten the life of circuit components. The single best approach to protecting the environment, the equipment and the operation is to prevent leaks and spills through good routine maintenance. A good preventative maintenance program will:

1. Increase productivity since equipment is utilized more,
2. Better utilize in-shop maintenance since there is less emergency work,
3. Improve control of spare part inventory and reduce parts usage,
4. Reduce equipment down time,
5. Reduce safety hazards,
6. Increase equipment life,
7. Reduce fines and clean-up costs due to environmental release, and
8. Reduce down time related to environmental release.

Oil spills

Even with the best maintenance program, there is still potential for a lubricant spill. There are increasing regulatory pressures from the EPA, Coast Guard and other environmental organizations. While small releases will not result in a Resource Conservation and Recovery Act (RCRA) clean up, large spills will. All petroleum fluid spills are "reportable events". These events involve a great deal of clean-up cost, administrative procedures and punitive fines that can range from tens of thousands to hundreds of thousands of dollars.

While spilling large quantities of biodegradable fluids is still considered under RCRA to be a reportable event, agencies are required to evaluate "biobased oils" differently than petroleum-based oils. As awareness of biodegradable fluid increases, state and federal agencies become more lenient regarding fines and clean-up costs. In fact, there are several case studies of equipment releasing several hundred gallons of vegetable-based hydraulic fluid into environmentally sensitive areas with no fines and minimal clean-up expense. In most instances, the operator was able to continue working while clean-up efforts were underway. Since the fluids were biodegradable and non-toxic, there was no long-term negative effect to the ecosystem.

There are several metrics to evaluate the extent of environmental compatibility. These include biodegradability level, eco-toxicity, bioaccumulation and base fluid classification.

Biodegradability

The ASTM 5864 defines *biodegradation* as "the process of chemical breakdown or transformation of a substance caused by organisms or their enzymes " (Section 3.2.3)

The ASTM 5864 defines *ultimate biodegradation* as "degradation achieved when the test substance is totally utilized by microorganisms resulting in the production of CO2, water, inorganic compounds, and new microbial cellular constituents (biomass or secretions, or both). (Section 3.1.13)

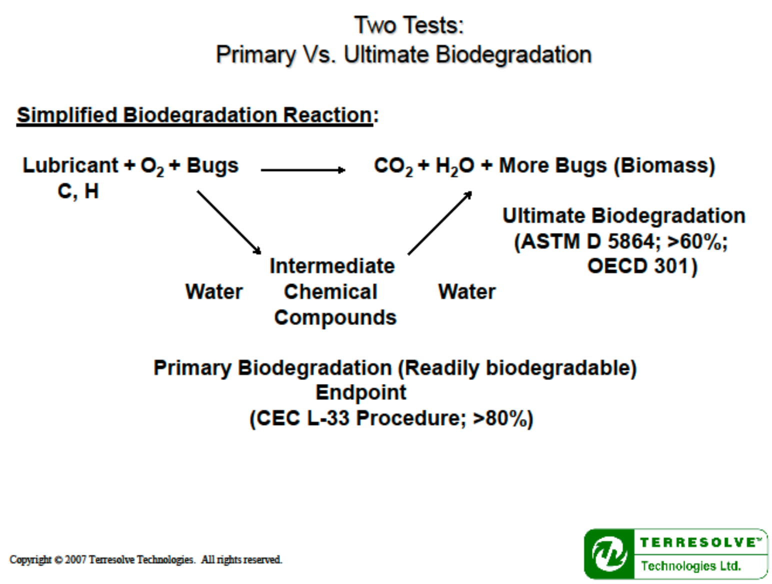

Figure 1. Measurements of Biodegradability

Shown in Figure 1 above, there are two commonly used measurements for biodegradation.
The first is "primary degradation" which measures reduction of the Carbon and Hydrogen bonds (C-H) in the initial solution; this is the reduction of the amount of the lubricant. The most widely used primary degradation test, was the CEC-L-33-A-93. This test has fallen out of favor in industry, however due to the vast quantity of data, it is still referenced regularly.

The second measurement of biodegradation is "secondary degradation" or "ultimate degradation". This measures the evolution of CO_2 through the biodegradation. The usual test for this is the OECD 301 or the ASTM D5864.

The ASTM D6046 has defined levels of biodegradability for both primary and secondary degradation as a function of degree of degradation, time, and test methodology.

Primary Degradation

Persistence Designation	Test Method	% Degradation Required	Days	Test Method
Pw (*Readily* Biodegradable)	Primary	80	21	CEC-L-33-A-93
Pw4 (*Inherently*)	Primary	<80	21	

Ultimate Degradation

Persistence Designation	Test Method	% Degradation Required	Days	Test Method
Pw1 (*Readily*)	Ultimate	60	28	ASTM D5864 OECD 301
Pw2	Ultimate	60	84	
Pw3	Ultimate	40	84	
Pw4 (Least Biodegradable)	Ultimate	<40	84	

Table 1. Biodegradation

It is essential that those with responsibility to market or select fluids for their biodegradability characteristics clearly understand the terminology, and be careful to avoid confusion within marketing literature. A common error has occurred wherein products have been assigned the "Ultimately Biodegradable" status, and described as having the 'highest biodegradability classification' per ASTM D5864

There are a few points that must be clarified, including:

1. As previously defined; "Ultimate biodegradation" is the evolution of the end product of biodegradation (CO2 and H2O mostly for lubricants). The ASTM 5864 clearly defines "ultimate biodegradation" as "degradation achieved when the test substance is totally utilized by microorganisms resulting in the production of CO2, water, inorganic compounds, and new microbial cellular constituents (biomass or secretions, or both). (Section 3.1.13)
2. ASTM D 5864 "Standard Test **Method** for Determining Aerobic Aquatic Biodegradation of Lubricants or their Components" is a test method, not a hierarchy.
3. ASTM D6046 – D2 "Standard Classification of Hydraulic Fluids for Environmental Impact" does create an environmental hierarchy. It does define "ultimate biodegradation" in section 3.1.22 which not surprisingly is the same as in the D5864 (see above).

There are two commonly used designations for biodegradability, "*readily*" and "inherently". *Readily* biodegradable is defined quantitatively above as breaking down rapidly in the environment by a defined amount in a specific time frame. *Inherently* biodegradable is misleading to the unknowing as it means "has the propensity to breakdown" with no defined amount or time frame.

Thus, an *inherently* biodegradable product breaks down very slowly over time, usually in terms of years. These types of products can persist in the environment for several years, continuing to cause substantial damage. They require long-term remediation due to the environmental persistence. Typically, these products are petroleum-based, like conventional lubricants. Chart 1 illustrates the difference in degradation timing of a *readily* biodegradable product compared to an *inherently* biodegradable product.

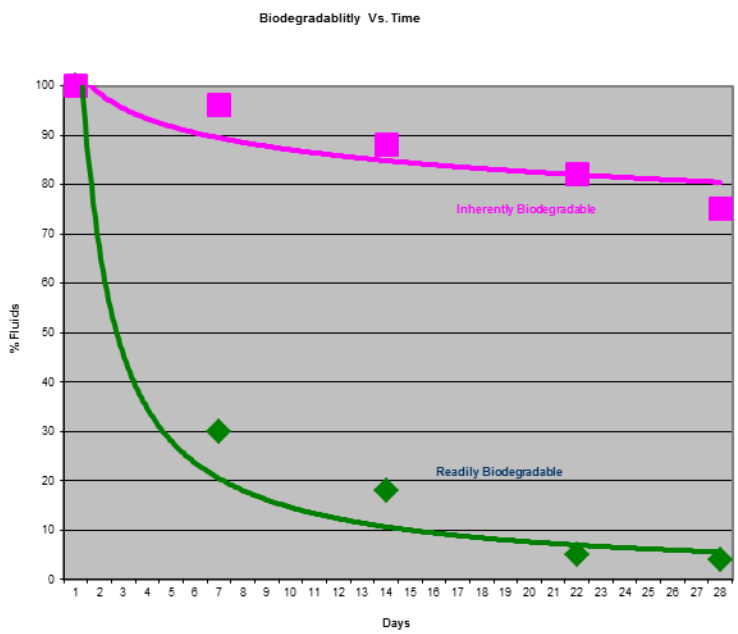

Chart 1.

Looking at Chart 1, it is easy to see the difference between a *readily* biodegradable product and an *inherently* biodegradable one.

Eco-toxicity

Another measurement to determine environmental effect of a lubricant is "eco-toxicity". Historically, tests for eco-toxicity have concentrated on the aquatic environment with a number of standard test procedures. Most typically, the tests are for "acute toxicity". This is a measurement of the concentration required to kill various organisms over a short period of time ranging 24-96 hours. Depending on the tests and its end points, the toxicity of a fluid is described by a loading rate in parts per million (PPM) of fluid that has a 50% effect (EL50) or causes 50% mortality (LL50) after the stated time. In other words, it defines the contaminant concentration at which one half of the sample organisms die.

The ASTM 6064 has defined levels of ecotoxicity as below.

Ecotoxicity in Soil	Ecotoxicity in Water	Loading Rate wppm (LL50)
Ts1	Tw1	>1000
Ts2	Tw2	1000-100

Ts3	Tw3	100-10
Ts4	Tw4	<10

Table 2. ASTM Ecotoxicity Classification

While the most benign level per the ASTM is 1000 part per million, well formulated environmentally preferable products can have LL 50 rating in excess of 10,000 ppm.

Base Fluid Classification

There are four main classifications of environmentally preferable fluids as defined by ISO 6743/4. They are HETG-vegetable based; HEPG-glycol based; HEES-ester based; and HEPR-PAO and other synthetic based.

Conventional Vegetable Based Fluids (HETG) – Early work in the field focused on lubricants made from vegetable oils (natural esters or HETG). Vegetable Based Fluids are readily biodegradable but their performance is most suited to cool and dry operating conditions. Equipment operators must take care to ensure that such parameter boundaries are not violated. HETG fluids can typically only withstand operating temperatures under 180°F-200°F. As a result, Vegetable Based Fluids, when exposed to heat, will oxidize rapidly and therefore will have a limited life expectancy. Another issue with the Vegetable Based Fluids is that they become unstable when exposed to wet environments or contaminated with water. These fluids should be utilized in light duty applications with controlled environments and relatively short change-out intervals.

Synthetic Esters (HEES)

The second phase of bio-development focused on Synthetic Esters (HEES). This classification of fluids is one of the most common synthetic biodegradables in the market. The strengths and weaknesses of synthetic esters are also well known and well documented.

Similar to Vegetable Based Fluids, Synthetic Esters are readily biodegradable. Synthetic Esters also perform well in standardized oxidation tests, which determine the life of the lubricant under test conditions. When new, clean, cool and dry, Synthetic Esters offer excellent performance.

Esters are synthesized by the reaction of a triglyceride (typically vegetable oil) with an acid and an alcohol. This reaction makes the ester and forms water and heat as by-product. Expressed chemically:

Vegetable Oil + Alcohol + Acid ↔ Synthetic Ester + Water + Heat

The double-headed arrow indicates that the reaction goes both directions. Therefore, when water is present, the reverse reaction occurs and is known as hydrolysis. This reforms the alcohols, acids and the triglycerides. In machine service, the acids can cause rust and wear, seal degradation, and corrosion to yellow metals. Consequently, ester based fluids must be maintained in a cool, dry state to obtain maximum performance. Consequently, because of harsh production environment (hot, wet, dirty), Synthetic Esters may not perform as well in some industrial applications, regardless of their biodegradability characteristics.

Poly Glycol (HEPG)

PAG fluids offer a wide range of performances and characteristics. Chief among them are the ability to absorb water and the ability to resist flame. This characteristic, however severely limits its use in some industrial applications since it draws water into the system and can create rust and wear. From a performance perspective, they are frequently incompatible with conventional materials and need special seals and filters. In addition, they are incompatible with conventional lubricants and a complete flush is required to change over. From an environmental perspective, if PAGs enter the environment, they will disperse in the water reducing the ability to clean up the fluids.

PAO Based Fluids (HEPR)

The remaining classification is the HEPR group. This classification embodies fluids derived from PAO base stocks, such as the Bio-olefin. One distinct advantage of PAO based fluids is that they can be tailor made to fit specific requirements. These fluids do not hydrolyze (break down when mixed with water) and, as such, they are much more stable in hot, wet conditions. Bio-olefins are typically compatible with Buna N, viton, and all common elastomers as well as adhesives used in filters. With stability, seal compatibility and biodegradability at a high performance level, a drawback is its high price base versus other fluids.

Class	Type	Base Fluid	Typical Performance	Seal & Hose Compatibility	Water Tolerance	Limitations	Application
HETG	Triglyceride (Vegetable)	Vegetable	Varies	Mixed	Medium	Water, Heat	Light Duty, Short change out, low temperature.
HEPG	Poly glycol (PAG)	Glycol	Weak	Very Poor	Miscible	Incompatible with many seal materials. Absorbs moisture. Prices vary	Fire hazard, specially designed system
HEES	Synthetic Ester	Synthetic	Mixed	Very Poor	Very Weak	Hydrolyzes in water. Creates acids. Expensive.	If dry, high performance.

HEPR	**PolyOlefin and others**	**Synthetic**	**Excellent**	**Excellent**	**Excellent**	**Expensive**	**Heavy duty, chance of contamination**

Table 3. Performance of Classes of Environmental Oils

Table 3, above, shows the various performance characteristics of the different classes of environmental fluids and where each should be utilized. From it, the reader can see the broad differences among the types.

Selection of Biofluids

There are a wide variety of performance levels among biodegradable products. Care must be used to select the right product for the right application. When an environmentally preferable product is required outside the common temperatures range, a biodegradable synthetic is usually required. While offering biodegradation, these products can operate in temperatures in excess of 400° F and still offer long fluid life. As would be expected, these products are significantly more expensive.

Care must be taken in choosing the appropriate product for the specific application. Responsible Environmentally Preferable Product (EPP) suppliers can clearly indicate their definition of “environmentally preferable”. The Federal Trade Commission has been very specific in their requirements for environmental claims and state “look for evidence that give some substance to the claim, the additional information that explains why the product is environmentally friendly”. Many “would be” EPP suppliers use misleading environmental claims such as “inherently biodegradable” or “food grade”. Suppliers should be able to support performance claims with test data. These data can include standard industry tests (ASTM), field-testing, and equipment manufacturer tests. Unless an EPP supplier specializes in environmentally preferable products, they are probably not expert in the field.

Summary

Millions of gallons of petroleum products are improperly disposed of or accidentally lost into the environment each year. Regulations are imposed on producers by federal, state and local authorities with increasingly costly penalties associated with these losses. Producers and users of lubricants are applying vigilance to reduce losses and reduce risk associated with eventual losses. There are multiple classifications of fluids that fit the biodegradability requirement that have varying degrees of performance. In an effort to improve environmental performance, industry must choose lubricants that can offer optimum long-term performance and environmental safety. The real proof of performance is how the fluids withstand the conditions under which they will operate.

Author
Mark Miller (better known as The Biodegradable Oil Guy) is the CEO of Terresolve Technologies, a Cleveland-based company that provides non-toxic, biodegradable lubricating products. Mr. Miller has a B.S. in Chemical Engineering from Tufts University and an M.B.A. from Manhattan College. He has engineered, sold and marketed lubricants and lubricant additives for over 30 years.

Terresolve Technologies, a Cleveland-based company, is dedicated to providing non-toxic, biodegradable lubricating products that deliver exceptional performance. For more information about Terresolve, field test results and all of its environmentally friendly products, visit their web site at www.terresolve.com or call (800) 661-3558.