Biodegradable Hydraulic Fluids: A Review

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ABSTRACT

There is currently increasing interest in biodegradable hydraulic fluids. Such fluids are often considered to include only vegetable oils, polyol esters and diester base stocks. However, other fluid base stocks including highly refined mineral oils, poly(alpha olefin) and fire-resistant fluids such water-glycol hydraulic fluids are also biodegradable fluid alternatives. This paper will provide an overview of the international literature on biodegradable fluids, various international testing protocol, fluid base stocks, effect of oxidative stability, material compatibility and pump performance. From the literature available, an assessment of future directions in this ever-changing field will be provided.

KEY WORDS

Hydraulic fluids, Biodegradable, Environmentally friendly

INTRODUCTION

Although mineral oils have traditionally been the most commonly used hydraulic fluids in the fluid power industry, they are being subjected to ever-increasing controls particularly due to the increasingly stringent governmental regulations regarding the impact of hydraulic fluid spill and fluid leakage on the environment. [1] Improper disposal, even if it is incidental, may be the source of large penalties or even litigation. [2]

European studies have identified hydraulic fluid leakage as one of the primary sources of ground water contamination.[3] This has been followed by a world-wide effort to identify hydraulic fluids which will exhibit reduced environmental and toxicological impact upon incidental contact with the environment. [4,5] (Note: The term "environmental impact" includes biodegradation, persistence and toxicity.)

There are a number of national environmental standards and labeling procedures being developed. [6,7] One of the first and most stringent environmental labeling procedures is the German "Blue Angel" label.[8] The purpose of this labeling procedure is to identify consumer products, including hydraulic fluids, that are not hazardous to the environment. An approved hydraulic fluid will require greater than 80% biodegradability in 21 days by the CEC-L-33-A-93 test or greater than 70% biodegradation by the Modified Sturm Test. All components must be non-polluting and conform to Water Hazard Class 0 or 1. [9]

Another program is the Environmental Choice Program of Canada. [9]. This program was initially developed to provide guidance for the disposal or reclamation of used industrial oil. [10] Interestingly, the term "EcoLogo" is used and not the term "environmentally friendly" because it was not intended to suggest those products with the EcoLogo were perfectly harmless to the environment. Very few products have NO impact on the environment. [10] However, the Canadian Environmental Choice program is being used to provide a criteria for the "environmental friendliness" of

industrial oils such as chain saw lubricants, hydraulic fluids and others. Note: The term "environmentally friendly" is used to denote those materials, which exhibit little "environmental impact."

In the USA, work is underway by the ASTM D.02 N.03 Subcommittee to establish a standard for the classification of environmentally friendly hydraulic fluids. However, instead of "environmentally friendly", these fluids will be classified as "eco-evaluated" (EE). [9,11], Also, the ASTM D.02 N.03 Subcommittee is working to establish standards for the classification and testing of eco-evaluated (EE) fluids.

In addition to basestock, a hydraulic fluid typically contains additives. Additives are used to enhance the fluid properties, which include antioxidant, antiwear, reduced foaming and improved air release properties. The presence of these additives affect hydraulic fluid biodegradation and toxicological properties.[12,13,14,15] Therefore, additive selection is of paramount importance.[16]

Thus far, the most commonly cited base stocks used for the formulation of "environmentally friendly" hydraulic fluids are either vegetable oils or synthetic esters [7,9,17]. The most common vegetable oils that have been identified for hydraulic fluid formulations are based on soybean oil, [18,19,20] rapeseed oil [21], and high oleic sunflower oil.[22] Canola oil is also used. The amount of unsaturation in a vegetable oil is climate-dependent. [22] For example, rapeseed grown in colder northern climates contains less unsaturation (canola oil) than when grown in warmer southern climates. This is important because the level of unsaturation affects physical properties and especially oxidative stability. For this reason, canola oil is one of the preferred vegetable oils for hydraulic fluid formulation. [22]

Work by Rhee, et. al. have shown that synthetic esters exhibit a number of advantages over vegetable oils such as a broader pour point temperature range, typically, -40°C - 150°C versus vegetable oil derived fluids which typically exhibit a temperature range of -10°C -90°C.[23] This limited range of operational temperatures for vegetable oils often renders them unsuitable for cold-weather applications.. Other workers have reported that in addition to a broader operational temperature range, synthetic esters provide substantial improvement in thermal/oxidative stability relative to vegetable oil based fluids.[24,25] The use of various vegetable oil derived hydraulic fluids has been published.[21, 26-29] Typically, either vane or piston pumps were used for performance testing. Although the antiwear results were generally good, these tests showed that vegetable oils exhibit poorer oxidative stability than mineral oil based hydraulic fluids. In view of the significant market pressures for the availability of "environmentally friendly" hydraulic fluids, most hydraulic pump manufacturers and many equipment suppliers have developed guidelines for the selection and use of these fluids.

[30-34]

Due to the variability of the performance of vegetable oil based hydraulic fluids that are currently available, some manufacturers appear to have developed their own privately labeled fluids to provide greater quality assurance.[33] Because of their favorable low temperature properties (pour point of -63°C), water solubility and fire resistance, hydrolube compositions provide a potential alternative to vegetable oils and synthetic esters as biodegradable hydraulic fluids.[35,36] Unfortunately, although there are numerous references describing various biodegradability properties of vegetable oils and to a lesser extent synthetic esters, there are considerably fewer analogous references for the biodegradability properties of hydrolube compositions using OECD GLP Principles (OECD, 1992a).[37] In some cases, it is not clear how the reported data was obtained or if it was previously published in other sources.

This report will provide a selected of biodegradation and toxicity data published for different classes of hydraulic fluids. The general subject of biodegradation and testing procedure will be discussed. Specific examples of published comparative test data will be provided, where available.

DISCUSSION

Biodegradable Fluids

Currently, soybean oil, because it is readily available in the USA, is being evaluated as a basestock for hydraulic fluid formulation.[19,20,26,38,39] In the biodegradable hydraulic fluid marketplace, rapeseed oil-based hydraulic fluid compositions may be referred to as "European fluids", and Canola oil-based hydraulic fluids may be referred to as "Canadian fluids".[40] There is a movement underway to make soybean oil-based fluids the preferred American biodegradable vegetable oil-based fluid composition.[40] The final class of hydraulic fluids to be discussed here is water-glycol fluids which are also known as hydrolubes.[41,42,43] While polyol esters and phosphate esters derive their fire resistance properties by either, or both, chemical structure and additives, hydrolubes derive their fire resistance properties from the presence of water in the fluid formulation.

1. Biological Degradation

There are various national standards currently that "biodegradability" and how it should be experimentally determined.[44-47] Two general classifications that are often used. One classification is based on the ultimate fate of the material after biodegradation. The other classification is based on the biodegradation rate. Wilkinson offered the following definitions [47].

a. Rate Definitions

Primary Biodegradation - This is a measure of the

conversion by biological systems of the original organic material into different products from the starting materials. This is not a measure of the biological impact of the substance but merely of the efficacy of the first step in what may be a long series of steps. In some cases, non-toxic substances which exhibit facile primary biodegradability can biodegrade into environmentally toxic materials!

Ultimate Biodegradation - This is often referred to as "mineralization" and is the complete conversion by biological systems of the original organic material into carbon dioxide, water and microbial biomass (and any inorganic ions, if present). [Note: Unfortunately, OECD methods and classifications do not recognize biomass incorporation.]

b. Rate Definitions

Ready Biodegradation - Substances which are classified as "readily biodegradable" exhibit greater than a certain fixed percentage conversion in a standard test [48]. This is usually measuring a parameter related to the degree of "ultimate biodegradation".

Inherent Biodegradation - The potential to eventually biodegrade - although at a rate lower than required for classification as "readily biodegradable". The OECD procedure also incorporates a "10 day window" which requires "that the percent theoretical CO₂ must reach 60% within 10 day after reaching the 10% level" [11] if the fluid is to be classified as biodegradable. This requirement applies for all of the OECD 301 methods. [Note: Based on their function, all of these "methods" would be more appropriately referred to as "screening procedures", not "testing" methods.] OECD is currently reevaluating this "10-day window" criterion because: this requirement is of questionable applicability to substances that are poorly water soluble.[11] and inherently biodegradable substrates may produce a time lag in the degradation process but still undergo ultimate biodegradation.[49] Therefore, this requirement appears to be unduly restrictive.

Experimental strategies involve the measurement of: a.) the amount of the original carbon consumed, b.) the consumption of oxygen used in the degradation test or c.) the evolution of carbon dioxide at the end of the biological degradation process. This is illustrated in Figure 3.[50]

Of the tests for "ready biodegradability", three of these are practiced most frequently: OECD 301A, 301B and 301E. [49] The criteria test for these tests are: [49]

b1. OECD 301A-AFNOR Test - This test is used for water soluble compounds that are relatively non-volatile and non-inhibiting to bacteria at 40mg/L dissolved organic carbon (DOC). The DOC of the test material is the sole source of COC for the aerobic microorganisms. The test

criteria is based on loss of DOC after 28 days.

b2. OECD 301B-Modified Sturm Test - This test is applicable for both water soluble and water insoluble compounds. Biodegradation is based on the yield of carbon dioxide produced over the 28 day duration of the test.

b3. OECD 301E-OECD Screening Test - This test is designed for water soluble, non-volatile and non-inhibitory compounds (5 - 40 mg/L DOC). This test also monitors the change in DOC with respect to time and is similar to OECD 301A.

One of the difficulties in conducting these aqueous tests is the insolubility of hydraulic fluids, with the exception of the water-containing fluids such as a water-glycol hydraulic fluid. Girling discussed this problem and the following procedures to enhance oil solubility: vigorous shaking, blending (Waring blender), homogenizing, ultrasonification, and chemical dispersion. [51] The factors which are known to influence the composition of the aqueous test media include: bulk fluid properties of the "OBP" (oil-based products), mixing environment, properties of the aqueous phase such as pH, water temperature, hardness, and salinity, physical and chemical properties of the OBP constituents and the OBP/water ratio [51].

These difficulties arguably skew BOD data in favor of water insoluble fluids because the % biodegraded substrate will increase as the solubility of the substrate decreases assuming the degradation rate remains unchanged. One way that this can be envisioned is by examining the effect of biodegradability rate on oil film thickness, which would presumably increase with increasing concentration and which should then result in lower degradation half-times. This was observed by Völtz [50]. Völtz also showed that the type and concentration of microorganisms that may be present in the aquatic environment also significantly affect biodegradation rates [50].

Biodegradation rates are often conducted by a number of possible tests. Two of the most commonly encountered tests are the CEC-L-33-A-94 test and the modified Sturm shake flask test. [11] The CEC-L-33-A-94 method is used to determine primary biodegradation (the first stage of degradation which corresponds to the initial changes in the molecular composition of the lubricant upon degradation, a useful screening test to assess the potential for degradation), The Modified Sturm Test is used to assess ultimate biodegradability where it is assumed that the lubricant components have completely "mineralized".

2. Published Biodegradation and Toxicity Data

a. **Aquatic Biodegradability** - Biodegradability, using the

CEC-L-33-A-94 test procedure, of various mineral oil basestocks was reported by Singh. These data show that mineral oil biodegradability is composition dependent. If aromatic, aliphatic and heterocyclic derivatives are minimized and the saturation level is increased, mineral oil derived compositions may be produced with biodegradability properties that rival vegetable oil and polyol esters. As expected, vegetable oil and polyol ester based fluids exhibited considerably higher biodegradation rates.[52]

In a different study, Kiovisky using the updated procedure CEC-L-33-A-94, also examined the effect of mineral oil base stock on biodegradability.[53] Hydrocracking produced relatively good biodegradation rates, approximately 80%. Naegely compared the biodegradability of white oils (25-45%) with typical ranges for vegetable oils (75-100%), polyol esters and diesters (55-100%) [22] Vegetable oils, as a class, undergo a relatively rapid initial biodegradation

b. Aquatic Toxicity - Toxicity (ecotoxicity) is defined as the "propensity" of the substance to produce adverse biochemical and physiological effects in a living organism. It incorporates both acute and chronic effect but does not include physical effects An acute effect is one which occurs after a short exposure to the test substance, short being some time period which does not constitute a large fraction of the life span of the organism. A chronic effect is one which occurs after a long contact with the test substance."[46] An example of a "physical effect" is the deprivation of a living organism of oxygen.

Comparative toxicity data on various biodegradable hydraulic fluids has been reported by Cheng.[29] Rainbow trout were used for the study under mechanical dispersion conditions to facilitate an oil water dispersion (since the oils evaluated were water insoluble). In general, none the basestock were determined to be toxic in this test.

c. Soil Biodegradability and Toxicity - Another area where there is relatively little biodegradation data for all classes of hydraulic fluids is on the fate and effects of biological degradation processes in soil.[55] Currently there are no international standards describing in-soil biodegradation testing procedures for hydraulic fluids. Also, there are relatively few soil biodegradation test results compared to aquatic biodegradation for the same series of hydraulic fluids. Völtz described the "Hamburg University Test" which measures CO₂ production (mmole CO₂ / 100g soil) after 7 days with 4% oil. In general, natural fats and oils are not persistent in the environment. In summary, although synthetic esters biodegrade faster in soil studies than mineral oil, they are still more persistent than a vegetable oil.

Haigh described the use of a 1 m² section of an agricultural field.[55] Oil added at concentrations varying

from 0.25 - 5.0 l/m² through an inverted test tube to a depth of 6 cm. Spring wheat, Broom variety, was planted. Seed germination (%) and growth rate (mm/day) was determined. The results of Haigh's work [55,56] showed that, as expected, synthetic esters are degraded more rapidly than mineral oil but not as rapidly as vegetable oil derived lubricant. In general, even vegetable oil requires ≥ 1 year for extractable residues to drop to levels comparable to the natural lipids present in the soil. The effects of these oils on growth rates varied from small reductions to complete inhibition. The degree of inhibition was not related to persistence of the oil residues. This means that it is important to monitor both biodegradation and toxicity.

3. Biodegradability and Toxicity Data for a Water-Glycol Hydraulic Fluid

Extensive biodegradability and toxicity data for a water-glycol hydraulic fluid has been reported. [36] This fluid exhibited 80% biodegradation after 28 days according to the OECD Modified Sturm test protocol 301B. [36] The acute oral LD₅₀ for rats was determined to be >20.0 g/kg. Dermal irritation determined on rabbits exhibited a Draize score of 0 which means it is not a skin irritant according to this test. Toxicity toward aquatic and terrestrial organisms was determined. The aquatic organisms that were tested included fish, invertebrates and algae. The terrestrial organisms included plants (radish) and invertebrates (earthworms). This water-glycol fluid was "practically non-toxic" to the aquatic organisms evaluated.

Current Specification Status

To date, there is no internationally accepted standard for determining the biodegradability properties of hydraulic fluids. Cheng, et. al. first proposed the following biodegradability criteria to determine if a lubricant would be acceptable for use in environmentally sensitive areas at the 1991 SAE Earth Moving Conference: [29] > 60% conversion to CO₂ in 28 days and aquatic toxicity for rainbow trout of > 1000 ppm.

However, there are a number of national standards under development that currently have various levels of international acceptance. These will be reviewed briefly in the next section.

Ecolabel Testing Requirements

1. German Blue Angel

The Blue Angel procedure developed in Germany incorporates a water hazard classification system which requires measurement of mammalian, fish and bacterial toxicity.[48] The Blue Angel requirement is dependent on the classification of the water hazard classification (WGK) number [48].

2. Canadian EcoLogo Testing Requirements

The Canadian EcoLogo is the most commonly encountered national environmental standard for hydraulic fluid use in North America. [59]

3. ASTM "Ecoevaluated" Testing Criteria

The ASTM D.02N.03 Sub-Committee is developing a testing criterion to evaluate the potential impact of the use of unused hydraulic fluids on the environment [59]. Since the standard is under development, the complete selection of required test methods is not yet firmly established. The current test method under development will only focus on environmental persistence and acute ecotoxicity [60]. Since only test methods for determination of aerobic fresh water have been developed to date [60], this new standard will be limited to the evaluation of unused hydraulic fluids in aerobic fresh water.

CONCLUSIONS

Although mineral oil based hydraulic fluids exhibit some of the best overall properties, they have two significant deficiencies; fire resistance and biodegradability which may preclude their continued use in many applications. While there is little that can be done about the poor fire resistance of mineral oils, except engineering or hardware modifications, biodegradability may be improved. In general hydrogen reduction or removal of aromatic compounds and increasing the overall paraffinic composition will improve aquatic biodegradability, but not to vegetable oil or synthetic ester levels. However, even highly refined mineral oil compositions are among the most persistent in soil biodegradability tests.

Two biodegradable alternatives to mineral oil based hydraulic fluids are vegetable oils and synthetic esters. They are more biodegradable than mineral oil. Of the two basestocks, vegetable oils are somewhat more biodegradable although that depends somewhat on molecular structure. In soil tests, vegetable oils are clearly more biodegradable. One vegetable oil, sunflower oil, although biodegradable, exhibited significant toxicity to seedling growth and yield.

Polyol esters, usually those based on trioleate esters of trimethylolpropane, exhibit excellent thermal stability relative to vegetable oils. Formulated fluids, although exhibiting excellent biodegradability, exhibit relatively poor soil biodegradability, a notable disadvantage in addition to their relatively higher cost.

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