Everything you ever wanted to know about the biodegradability of lubricants and greases

***Vincent Bouillon**, Eurofins BFB Oil Research S.A; Les Isnes (Gembloux); Belgium*

We all agree that sustainability is relevant to the lubricants industry. Sustainability efforts are well underway and lubricants are part of the solution. A lubricant's potential to reduce friction and wear, prevent overheating, reduce energy consumption and increase the lifetime of equipment is of great benefit to the industries which use lubricants, as well as to the lubricant industry itself.

In spite of that, we can't forget that lubricants may be harmful and dangerous and may cause long-term adverse effects on biota.

A small drop of lubricant can contaminate a large quantity of groundwater and render it undrinkable. Despite the efforts being made to recover, regenerate and re-refine lubricants, it is recognised that more than five million tons of lubricants are not collected and are disposed of in the environment.

Biodegradable substances may be removed from sewers, sewage treatment plants, or the environment directly, preventing them from reaching groundwater. This makes biodegradability one of the most important intrinsic properties of substances when determining their potential environmental hazard.

Why you need to evaluate biodegradability

The biodegradation of organic chemicals influences exposure and, hence, is a key parameter for estimating the risk of long-term adverse effects on the environment. This is why data on biodegradation is requested in many regulations, directives, acts, labels (VIDA, VGP, EEL, DSD, DPD, CLP, REACH, GHS, WGK, SDS and LCA).[1]

General testing strategy for biodegradability

An adopted approach allows chemical biodegradability testing to be organised into a general testing strategy that follows three steps:

- First, the aerobic biodegradability is assessed in a screening test for ***ready biodegradability***.
- If the result of the ready biodegradability test is negative, an examination using a ***simulation test*** may be carry out to obtain data describing the biodegradation rate in the environment. Alternatively, or in addition, a screening test for ***inherent biodegradability*** may be conducted in order to generate data describing the potential biodegradability under optimised aerobic conditions, such as in sewage treatment plants.
- Finally, the ***potential biodegradability*** under anoxic conditions may be examined in a screening test for anaerobic biodegradability.

[1](https://www.lube-media.com/oil-industry-abbreviations/), Ed

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Use the right term

Many terms are associated with biodegradability: primary, ready/readily, ultimate/ultimately, potentially, inherently, simulation test, and abiotic transformation. These are all related to test methods and their meanings are clearly defined in OECD (Organisation for Economic Co-operation and Development) guidelines.

The ***primary biodegradation*** is the alteration in the chemical structure of a substance, brought about by biological action, resulting in the loss of a specific property of that substance. The laboratory tests which are carried out to evaluate primary biodegradation are mainly based on specific analysis of test substance die-away or concentration of intermediate substances formed. Though informative, a positive test result cannot, however, be considered as proof that the test substance will rapidly biodegrade in the environment.

In *inherent*, *potential*, and *intrinsic* biodegradability tests, degradation has a high chance of taking place. These test procedures allow prolonged exposure of the test substance to microorganisms and a low ratio of test substance to biomass, which offers a better chance of obtaining a positive result. Some of these tests may also be conducted using microorganisms that have previously been exposed to the test substance, which frequently results in adaptation, leading to a significant increase in the degradation rate. Because of the favourable conditions employed in these tests, rapid biodegradation in the environment of inherently biodegradable chemicals cannot generally be assumed.

Ultimate, *ready*, and *easy* aerobic biodegradation refers to the level of degradation achieved when the test substance is totally utilised by micro-organisms, resulting in the production of carbon dioxide, water, mineral salts and new microbial cellular constituents (biomass).

These tests are so stringent that positive results are unequivocal, and it may be assumed that the chemical will undergo rapid and ultimate biodegradation in the environment. In such cases, no further investigation of the biodegradability of the chemicals is normally required.

Simulation biodegradability tests simulate degradation in a specific environment with realistic conditions (indigenous biomass, temperature, soil, sediments or surfaces which allow the sorption of the chemical and a low concentration of test substance). Biodegradation is measured either by radiolabelling techniques or by specific chemical analyses.

Frequently, an important step during the degradation of chemicals in the environment is the ***abiotic degradation***, which includes oxidation, photolysis and hydrolysis. Although abiotic transformation in itself is only primary degradation, the products formed by such abiotic processes may be biodegraded further by microorganisms.

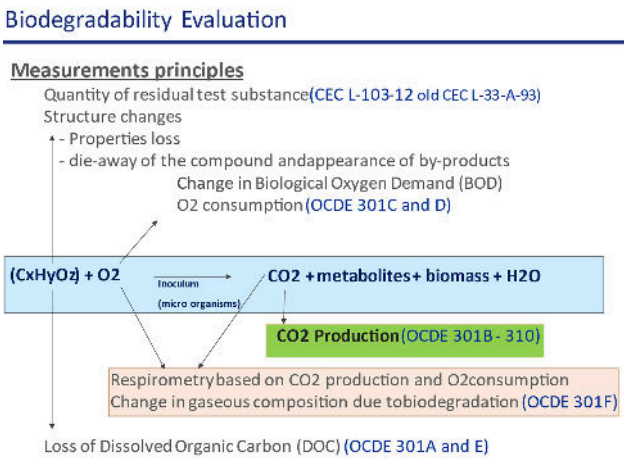
Biodegradability principle and test methods

A solution, or suspension, of the test substance in a mineral medium is inoculated and incubated during 28 days under aerobic conditions in the dark or in diffuse light.

The amount of dissolved organic carbon (DOC) in the test solution due to the inoculum should be kept as low as possible compared with the amount of organic carbon due to the test substance. Allowance is made for the endogenous activity of the inoculum by running parallel blanks with inoculum but without test substance, although the endogenous activity of cells in the presence of a chemical will not exactly match that in the endogenous control.

A reference compound is run in parallel to check the operation of the procedures.

In general, degradation is followed by the determination of parameters such as ***loss of DOC, CO_2 production and oxygen uptake and respirometry;*** with automatic respirometers, the measurement is continuous. DOC is sometimes measured in addition to another parameter, but this is usually done only at the beginning and end of the test. Specific chemical analysis can also be used to assess primary degradation of the test substance and to determine the concentration of any intermediate substances formed.



Complementary information on the biodegradability of lubricants

The most appropriate test method for lubricants and greases

Lubricants and greases are generally poorly water-soluble organic compounds which are classified as difficult test substances and require an appropriate mode of preparation in order to achieve reliable test results.

First, the possible test methods are restricted to CO_2 production (OECD 301B or equivalent test methods) and Repirometry (OECD 301F or equivalent test methods).

Regarding respirometry, the formula of the test substance and its purity, or relative proportions of major components, should be known, so that the ThOD (Theoretical Oxygen Demand) can be calculated. Sometimes, if the ThOD cannot be calculated because the test material is insufficiently defined, the COD (Chemical Oxygen Demand) value may be used to calculate the percentage degradation, but you must keep in mind that this can lead to erroneous results.

The most appropriate biodegradability test method on lubricants and greases is based on CO_2 production; this is the parameter adopted for the recent test method EN 17181, dedicated to fully formulated hydraulic fluids, which also includes the best mode of preparation.

Best mode of preparation

ISO 10634 is guidance for the preparation and treatment of poorly water-soluble organic compounds for the subsequent evaluation of their ultimate biodegradability in an aqueous medium.

Some introduction techniques are proposed, such as direct addition, ultrasonic dispersion, adsorption on inert support, and the use of emulsifiers or non-biodegradable solvents.

Carrying out biodegradability tests on lubricants and greases requires an introduction technique which facilitates the bio-availability of the test substance, reduces the adsorption on the test flask walls, doesn't change the chemical structure (ultrasonic dispersion), avoids any contamination from the support and interference of a solvent or emulsifier, and maintains homogeneity as far as possible.

The best technique for oils and greases is therefore introduction through adsorption on an inert support, followed by evaporation of the volatile solvent used.

Factors which influence aerobic biodegradation

Some factors may affect aerobic biodegradation:

- Branching of hydrocarbon chains
- Length of hydrocarbons chains & molecular weight
- Unsaturation
- Toxicity against micro-organisms
- Oxygenated compounds.
- Stability (Photolysis – Hydrolysis - Volatility)
- Presence of substrate (support - binding sites)
- Ambient conditions :
  (Temperature, Pressure, Luminosity, Medium, Presence of nutriments, pH)
- Interfacial tension with water
- Effectiveness of the micro-organisms (enzymatic capacity for the substance to decompose, adaptation of micro-organisms)
- Water solubility
- Heterogeneity

Scope and restriction of test methods

OECD guidelines specify that generally, biodegradability tests are intended for pure chemicals; nevertheless; ***it is relevant to examine the ready biodegradability of mixtures of structurally similar chemicals, like oils*** and surface-active substances (surfactants). Such substances often occur as mixtures of constituents with different chain lengths, degree and/or site of branching, or stereo-isomers, even in their most purified commercial forms. REACH describes UVCBs, i.e., substances of ***unknown or variable composition, complex reaction products or biological materials***.

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Biodegradation tests on fully formulated lubricants are relevant due to the high number of single components, which make testing each individual component costly and impractical.
Moreover, the lubricant formulation is a mixture of base oils with some additive packages. It's very unusual that the additives manufacturer provides the pure active substance, which will have a different chemical structure that the base oil in which it is diluted; so, the same situation with the additive package and with the formulated lubricants arises.

We must also remember the scope of application of the biodegradability test methods, which forbids carrying out the test at a concentration that is toxic for the micro-organisms. If you consider the lubricant as a single component, taking into account the concentration of the active additive substance in the lubricant and the test concentration, the additive molecules may not be toxic while testing the fully formulated lubricant.

Finally, in relation to eco-toxicity, if the lubricant is in contact with the environment, this concerns the entire lubricant and not single components. The test methods applicable to lubricants and greases, based on CO_2 production and O_2 consumption, require that the Total Organic Carbon (TOC) and the Theoretical Oxygen Demand (ThOD) respectively are known.

The scope of application for both methods is limited to organic compounds which are not toxic for micro-organisms at test concentration. Moreover, the inoculum must not come from industrial sewage treatment, nor be pre-adapted (pre-exposed) to the test substance.

Test methods based on CO_2 production are not applicable to volatile compounds and those which contain more than 5% of inorganic carbon (like carbonates) within the total carbon content.

Test validity

A test is considered valid if:

- The reference reaches the pass level at day 14
- In case of toxicity test, the biodegradation is above 25% at day 14
- The difference between replicates at the plateau (or the end of the 10-d window) is lower than 20%
- The cumulated CO_2 content from the inoculum and air is lower than max 40 mg

Test uncertainty

Biodegradability tests use biological materials composed of inoculums from different sources and origins and which are not normalised. This is certainly one of the key reasons for results variation.

Poorly water-soluble organic compounds also require various modes of preparation, which further increases variation.

The accumulation of uncertainties of analytical determinations from the pre-requested data to the 28-day end period further impacts test variation and leads to a reproducibility as high as 30%.

It is worth noting that variation is smaller for test substances which present high or low biodegradation results.

To limit variation, the best practice for comparing the biodegradability of many test substances is to carry out the tests in the same series, using the same inoculum and the same mode of preparation; in this case, test variation can usually be reduced to less to 10%.

Interpretation of test results

Threshold level

The duration of 28 days for ready biodegradability tests was defined in order to allow sufficient time for the microorganisms to adapt to the chemical.
The pass level for theoretical carbon dioxide ($ThCO_2$) and for theoretical oxygen demand (ThOD) is 60%; this level is considered evidence of ready biodegradability.

According to OECD guidelines, reaching the pass level means it may be assumed that the chemical will undergo rapid and ultimate biodegradation in the environment.

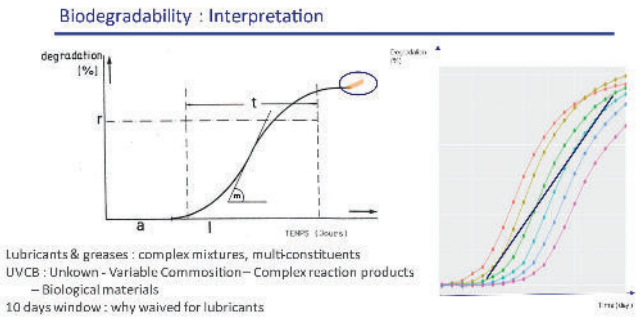
Biodegradation above 20% may be regarded as evidence of inherent, primary biodegradability. When results of ready biodegradability tests indicate that the pass level criterion is almost fulfilled (i.e., ThOD or $ThCO_2$ slightly below 60%), such results can be used to indicate inherent biodegradability.

The pass level of 60% (O_2 demand or CO_2 evolution) may seems to be a low value, but it demonstrates complete mineralisation, as the remaining carbon of the test substance is assumed to be built into the growing biomass.

Theoretical curve and the 10-day window

For pure substances, the theoretical biodegradation curve starts with a lag phase, which is the period from inoculation until degradation has increased to about 10%. The lag phase is followed by the degradation phase, which is the time from the end of the lag period to the point at which 90% of the maximum level of degradation has been reached (the plateau).

The 10-d window is the 10 days immediately following the 10% of biodegradation, i.e., from the end of the lag phase.



The general requirement for all ready biodegradability tests is that the pass level is achieved within the 10-day window. ***Nevertheless, the 10-day window criteria may be waived for complex (UVCBs), multi-component substances and the pass level is raised to 28 days***. It is anticipated that sequential biodegradation of the individual structures is taking place, leading to a curve without an inflexion point, making the 10-day window unsuitable.

A case-by-case evaluation should, however, take place as to whether a biodegradability test on such a substance will give valuable information regarding its biodegradability or whether an investigation into the degradability of carefully selected individual components of the complex, multi-component substance is required instead.

Conclusion

Biodegradation is a key parameter for estimating the risk of long-term adverse effects on the environment.

The term ***ultimate***, ***ready*** or ***mineralisation*** must be used only when the final stage of degradation is reached, resulting in the production of carbon dioxide, water, mineral salts and new biomass; a positive result (pass level) assumes that the chemical will undergo rapid and ultimate biodegradation in the environment.

UVCBs, lubricants or greases are specific matrices for which the best method is based on CO_2 evolution and the best mode of introduction is adsorption on inert support.

Many factors influence biodegradability, and even if test conditions in a laboratory test try to reduce these, the uncertainty remains high. The best way to limit test variation and to compare some compounds is to carry out the biodegradation tests in the same laboratory, using the same inoculum.

The 60% pass level may seem like a low value but it demonstrates large mineralisation because a part of the carbon from the test substance is used for biomass growth.

The biodegradation curve for UVCBs, lubricants and greases are usually not similar to the theoretical curve with the lag phase, the degradation phase and the plateau; this is due to the sequential biodegradation of the individual structures, leading to a curve without an inflexion point, which is why the 10-day window should not be applied.

References

[1] OECD Harmonised Integrated Classification System for Human Health and Environmental Hazards of Chemical Substances and Mixtures. OECD Series on Testing and Assessment. No. 33.

[2] OECD Guidelines for the Testing of Chemicals, Section 3 Degradation and Accumulation, Ready Biodegradability, 301Adopted: 17.07.92.

[3] OECD Guidelines for the testing of chemicals, Section 3 Part 1: Principles and strategies related to the testing degradation, of organic chemicals, Adopted 23 March 2006.

[4] United Nations Economic Commission for Europe – annex 9 "Guidance on hazard to the aquatic environment". 2017.

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