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Studies on biodegradability of bio-based lubricants

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ABSTRACT

Vegetable or synthetic lubricants, also called biolubricants, are less harmful to the environment. In order to quantify their biodegradability, some tests are able to predict how long oil/lubricants will take to be degraded in the environment. This study proposes to evaluate the biodegradability of bio-based lubricants using a bio-kinetic model (without microorganisms), comparing their performances with fresh vegetable oil and mineral oil. The results are presented through an *Effective Composition for Biodegradation* (*ECB*), half-lives and biodegradation time profile. The synthesized biolubricants showed ECB values closer to vegetable oil than mineral oil. Half-life times are approximately 12 days for fresh vegetable oil, around 20–30 days for the biolubricants, and over 200 days for the mineral oil.

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1. Introduction

Biodegradability is an important characteristic for the majority of today's chemical industry products, and represents a way of measuring the risk level of decomposition presented by these products when deployed to the environment. Biodegradation is a natural process caused by the action of microorganisms, in the presence of oxygen, nitrogen and minerals.

In the process of formulating lubricant oils, biodegradability is strongly dependent on the oil used. Basestock oils and finished lubricants are products with a potential risk of being in direct contact with the environment, which may happen in their production, distribution, services usage or even in disposal after their utilization. Therefore, environmental authorities have been increasingly demanding less toxicity in these products, so they will cause less harm to the nature [1–3].

The impacts on the environment caused by inappropriate disposal of the wastes are huge. Lubricants, when in intentional or accidental contact with the soil, make it useless for farming and civil construction, killing the vegetation and the microorganisms [4,5]. Brazilian Environmental National Council (CONAMA) determine that the best environmental management for used or contaminated oils is re-refining and, for that, there are many companies properly registered in this Council that are able to perform this activity [6].

Some kinds of lubricants are more risky to be in contact with the environment and because of that they must be preferably formulated with less environmentally toxic and more biodegradable products. Some pathways are already being explored such as: chainsaw oil, drilling fluids and lubricants for the train line. Other applications of highly biodegradable lubricants are in services that may contain leaking risks, like forest and mining equipment and in very sensible areas like platforms, agricultural equipment and hydroelectric power plants. However, environmental agencies have been trying to put more restrictions to all the products with low biodegradation rate, whether they are used for risky applications or not. The intention is that when these products get in touch with the environment, accidentally or not, they may be quickly isolated and treated [7–9].

Nowadays, there are plenty of evaluation methods of biodegradability. Most of them use microorganisms to obtain the data, even though they are difficultly adjusted and long time methods. The analysis methods of biodegradability without using microorganisms are relatively recent and were based on the oils components and their degradation reactions [10]. However, it is still not clear what is the criteria to determine if certain basestock oil is biodegradable or not, that is, what quantity of sample will biodegrade and how long it will take, yet the evaluation of the biodegradability is an important tool of comparison between two different lubricants.

2. Standard methods

One of the first methods proposed to evaluate the biodegradability of lubricant oils and fuels was the CEC L-33-T-82,

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established by the Co-ordinating European Council (CEC). The method uses a standard fluid of known biodegradability where both, the standard and the sample are inoculated with microorganisms. The progress of the reaction is accompanied by infrared throughout a period of 28 days. This was the most used and known method by biolubricants producing companies in years. Over the years, this method has not passed through many changes and was updated to the method CEC L-33-A-94 which stipulated that a biodegradable sample, by definition, would have to be 80% consumed in 21 days [11].

Another way of monitoring these reactions is the quantification of carbon dioxide released from decomposition, since the reactions of biodegradation form CO_2 and water at the end of the process. This point of view was adopted by American Society for Testing and Materials (ASTM) with the ASTM D5864-11 [12] method (Standard Test Method for Determining Aerobic Biodegradation of Lubricants and Their Components), which simulates a natural aqueous environment of biodegradation and quantifies the production of CO_2. According to this method, ASTM labels a sample as fully biodegradable if 60% of that sample has been completely converted to CO_2 over a period of 28 days [3,13,14]. With this same concept of monitoring, there were several other methods with different forms of analysis of CO_2 and different criteria for judging the biodegradability of the sample.

The method developed by the Organization for Economic Cooperation and Development (OECD) is also based on the CO_2 production by the sample's biodegradation. The CO_2 is captured in a sodium or barium hydroxide solution which is then titrated and the amount of CO_2 emitted is quantified. A biodegradable sample must exhibit, in a period of 28 days, a consumption greater than or equal to 60% of the initial sample. In order to measure the ultimate stage of the aerobic biodegradation process, the OECD 301 B method is used in aqueous or soil medium as an ultimate biodegradation test [15]. Another developed method is the Bartha Respirometer Method. In this method, the produced CO_2 is captured by a KOH solution. The result of this method is a graph expressing the quantity of CO_2 produced as a function of the analysis time [3,16].

2.1. Bio-kinetic method

The difficulty of working with microorganisms combined with the long time taken on the analysis led Rhee (2005) [10] to develop a method capable of estimating, rapidly and reliably, the biodegradability of a lubricant sample without the use of microorganisms.

Although there are many methods for this purpose, few results were similar to those reported by ASTM D5864-11 [12], adopted as consistent for this assessment. The use of a bio-kinetic model (equations for biomass growth, such as Monod – details in Ref. [10]) and the knowledge about the biodegradation process for oils led them to obtain correlations to estimate half-life and calculate the cumulative biodegradation consistent with the ASTM D5864-11 [12] method.

The oil biodegradation depends on its chemical composition. The saturated chains are easily attacked by microorganisms and tend to biodegrade. However, aromatic and polymeric chains are unlikely to be attacked by microorganisms and are more resistant to biodegradation [10,17].

From the work published by Rhee (2005) [10], it was developed a standard method to evaluate the biodegradation of base oils and lubricants without the use of microorganisms (ASTM D7373-12 [18]). Since this is considered a recent method, not many researchers have studied biodegradability using this approach. However, Luna *et al.* (2010) [19] reported the use of this bio-kinetic model to estimate and compare the biodegradability of mineral, vegetable and synthesized oils, where the method performed well showing a half-life of 25 days for the synthesized oil, presenting a considerable higher biodegradability when compared to mineral oils. In this context, Silva *et al.* (2013) [20] compared the biodegradability of two lubricant base fluids from castor biodiesel esters, using two different catalysts, tin and sodium methoxide, concluding that the presence of tin may decrease the oxidative stability and biodegradability of such products.

Beyond the ASTM D7373-12 [18] method, other studies have reported different ways of measuring biodegradability, for example the use of a lysimeter to follow the migration and progressive primary biodegradation of lubricants [14]. Another approach is the use of mathematical models along with experimental data to predict how different types of oils may affect the parameters in biodegradation kinetics [21].

This study proposes to evaluate the biodegradability of two different bio-based lubricants from castor oil and compare their performances with samples of mineral oil and pure vegetable oil, using bio-kinetic tests.

3. Materials and methods

3.1. Materials

Samples of mineral oil were provided by Petrobras (Brazil) and the vegetable oil used for this study was commercial castor oil from Proquinor (Brazil). Physicochemical properties of these samples are reported in Table 1. Ricinoleic acid (> 98 wt%), obtained from castor oil, was kindly supplied by Miracema-Nuodex (Brazil). Analytical-grade reagents (n-pentane, toluene, diethyl ether anhydrous, acetic anhydride and ethyl alcohol) were from J.T. Baker (USA). 2-Ethyl-1-hexanol (> 99.6%), 1-octanol anhydrous (> 99%) and boron trifluoride diethyl etherate were from Sigma-Aldrich (USA). Silica gel (70–230 mesh) and activated bauxite (20–60 mesh) were supplied by Macherey-Nagel (Germany) and Curimbaba (Brazil), respectively.

3.2. Preparation of bio-based lubricants

Two different biolubricants were synthesized and coined as BL*x*, where *x* is related to the alcohol used in the esterification step (1 for 2-ethyl-1-hexanol; *2* for 1-octanol), as depicted in Figs. 1 and 2. The esterification reactions were conducted with ricinoleic acid in a batch reactor (200 mL) maintained at 80 °C for 24 h under inert atmosphere. Acid/alcohol molar ratios were 1:1.2 for 2-ethyl-1-hexanol, and 1:2 for 1-octanol. All esterification homogeneous reactions were catalyzed by boron trifluoride diethyl etherate (0.5 wt%). The acetylation reactions were performed with acetic anhydride using an alkaline catalyst (KOH, 5 wt%). The reaction was carried out homogeneously in liquid phase at 90 °C for 12 h under inert atmosphere and intense stirring. The products were purified using a Kugelrohr distiller under high vacuum at 110 °C to remove excess alcohol. After separation, the products were

Table 1
Physicochemical properties of vegetable and mineral oils.

Samples	Specific gravity at 20 °C (g/cm³)	Pour point (°C)	Flash point (°C)	TAN (mg KOH/g)	Viscosity (cSt)		VI
					40 °C	100 °C	
Castor oil	0.958	−15	286	1.120	261.3	19.6	84
Mineral base-stock oil	0.892	−33	162	0.001	19.9	4.8	174

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