We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

CLARIVATE ANALYTICS

BOOK CITATION INDEX

INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Biodegradable Lubricants and Their Production Via Chemical Catalysis

José André Cavalcanti da Silva
Petróleo Brasileiro S.A. – Petrobras / Research Center – CENPES
Brazil

1. Introduction

The primary purpose of this chapter is to describe the differences among biolubricants and petroleum-based lubricants, especially their production and physical and chemical properties. Established production methodology will be described, especially those using chemical catalysis that have been developed at the laboratories of the Petrobras Research Center (CENPES), in Rio de Janeiro, Brazil.

Today there is growing concern about the future availability of petroleum-based products. In addition, millions of tons of lubricants are dumped into the environment through leakage, exhaust gas and careless disposal. Some of these wastes are resistant to biodegradation and are threats to the environment. Thus, there are two major issues confronting the lubricant industries today: the search for raw materials that are renewable and products that are biodegradable.

The oleochemistry represents a significant challenge to biolubricants production by petroleum companies. All the required technologies from seed crushing to oil refining, fractionation and chemical transformation are in place. The main research emphasis has been placed on ways to produce biolubricants with suitable viscosity and liquid-state temperature range. In addition, these lubricants must not corrode the machinery they lubricate and they must be stable under the conditions of their use. These requirements eliminate many simple fatty acid esters. Saturated esters with long enough chains to not be too volatile or lacking in viscosity are solids in the temperature range required by many lubricant applications. Double bonds will lower their melting point but introduce instability to oxygen attack, especially for the typical polyunsaturated fatty acid found in most vegetable oils. Branching will reduce the melting point but such fatty acids are relatively rare in nature. The solution to these problems that will be described on this chapter emphasizes the use of Brazilian raw materials. The well-developed Brazilian program of biodiesel production from soybean and castor oils has led to the choice of ricinoleate esters as potential biolubricant ingredients.

2. Castor and its derivatives

Castor oil is produced in the seed of the castor oil plant, *Ricinus communis*, and has been used for medicinal purposes for many years. During the 20th century, a number of industrial uses were developed including its use as a lubricant (Azevedo & Lima, 2001).

Castor oil was introduced into Brazil by the Portuguese for use as in illumination and as a carriage shaft lubricant. The climate of Brazil is suitable for growing castor plants and it can be found today among the wild flora in many parts of Brazil as well as a drought resistant cultivated plant.

From its seeds industrialization is obtained, as main product, the oil (47%) and, as by-product, the castor waste that may be used as a fertilizer.

Castor oil posses unusual and has greater density, viscosity, ethanol solubility and lubricity compared with other vegetable oil. This oil also has a wide chemical versatility inside the industry, due to be used as raw material to the synthesis of a large amount of products.

Furthermore, we can obtain biodiesel from castor oil, which replaces the petroleum-derived diesel as fuel. Besides, this oil posses the unusually fatty acid, ricinoleic acid, which makes about 90% of its composition. Ricinoleic acid is similar to the common fatty acid, oleic acid, except it has a hydroxyl group on the 12th carbon of its 18 carbon chain. Like oleic acid, ricinoleic acid has a *cis* double bond between the 9th and 10th carbon, as can be seen in figure 1.
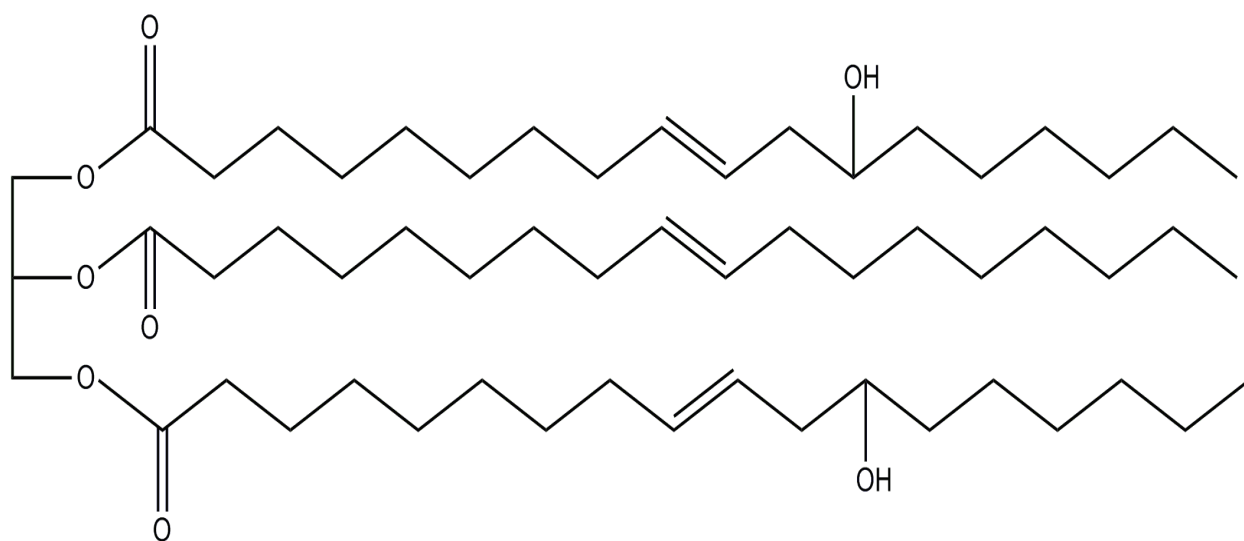

Fig. 1. Castor oil molecular structure (*Ricinus Communis*)

Table 1 presents the main physical-chemical characteristics of this oil.

Property	Value
Iodine Index	84-88
Viscosity at 100°C	20.00 cSt
VI (Viscosity Index)	90
Melting Point	-23°C
Ricinoleic Acid Content	90%
Linoleic Acid Content	4.2%
Oxidative Stability by RPVOT	25 Min.

RPVOT: Rotary pressure vessel oxidation test.

Table 1. Typical castor oil physical-chemical characteristics

The hydroxyl group of castor oil increases its polarity and makes it a better solvent for lubricant additives than other vegetable or mineral oils. Besides, castor oil presents high viscosity and low pour point, but its viscosity index is lower than the others vegetable oils, which means that its viscosity changes more with temperature than the other oils.

Castor oil has been used on the manufacturing of more than 800 products, ranging from bullet-proof glasses, contact lenses, lipsticks, metal soaps, special engine and high rotation reactors lubricants, high resistance plastics, polyurethanes, etc. Its odd properties give lubricity to the mineral diesel, like sulfur, becoming a special oil in the current world market.

The major castor seeds and oil producing nations in order of their production are India, China and Brazil. Germany and Thailand are the greatest castor beans importers (94%), but the United States consumes the most castor oil.

The state of Bahia produces 85% of Brazil's production of castor oil, being together with the state of Minas Gerais, the states where are located the main oil extraction companies. Brazil produces about 160,000 metric tons of beans per year. As the internal consumption of castor oil is small (10,000-15,000 metric tons per year), there is an excess of about 45,000-50,000 metric tons per year for export.

3. Base oils

The term "base oils" refers to the various oils used in the world's technological applications. This chapter will focus on lubricant oils. The base oils are the larger proportion constituents at the lubricants formulations and most of them are derived from petroleum. They can be classified as mineral or synthetic oils, depending on their production history (Lastres, 2003).

The first known lubricants used by humans were animal and vegetable based oils. In the 19th Century, the natural triglycerides were replaced by petroleum based oils, called mineral oils. In some lubricants applications, certain performance standards are required that cannot be met by conventional mineral oils. Alternate processes have been devised for their production usually to achieve greater durability or lower environmental impact. Vegetable oils are less expensive than minerals and are produced from renewable resources.

Mineral oils are produced through the petroleum distillation and refining. They are classified in paraffinics, naphthenics and aromatics, depending on the hydrocarbon type predominant in its composition. They possess 20 to 50 carbon atoms, on average, per molecule, and these can be paraffinic chains (linear or branching alkanes), naphthenic chains (cicloalkanes with side chains) or aromatic chains (alkyl benzenes), as illustrated on the figure 2.

The paraffinic base oils owe high pour point and viscosity index. To produce them, the dewax step is very important and the product, even dewaxed, still needs to be additivated with a pour point depressor to avoid the wax crystals growth at low temperatures and to reduce the product flow temperature.

The naphthenic base oils possess higher levels of carbons in cycle chains (naphthenics) than the paraffinics. The cut of a naphthenic petroleum has low linear wax levels and does not need to be dewaxed. Its pour point can achieve -51°C (base oil NH-10). On the other hand, they have low VI values (becoming very hard their usage on the engine oil formulations). They are more used on the formulations of cutfluids, shock absorbers oils and as isolation fluid to electrical transformers. The aromatic oils are used as extensor oils at the rubber industry.
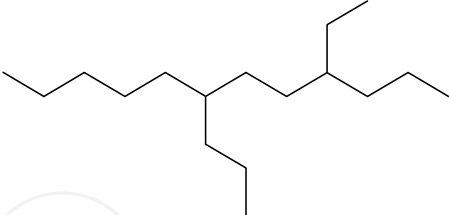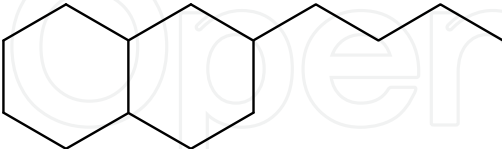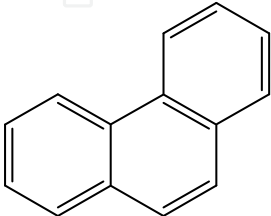
Oil type	Carbon chains type
Paraffinics	
Naphthenics	
Aromatics	

Fig. 2. Structure of the mineral oils composition

CATEGORY	SATURATES (¹)		SULFUR, %P (²)	VISCOSITY INDEX (³)
GROUP I	< 90	and / or	> 0.03	80 - 120
GROUP II	≥ 90	and	≤ 0.03	80 - 120
GROUP III	≥ 90	and	≤ 0.03	> 120
GROUP IV	POLYALPHAOLEFINS (PAO)			
GROUP V	OTHER BASE OILS NOT INCLUDED ON THE GROUPS I, II, III and IV			

(¹) ASTM D 2007
(²) ASTM D 2622 or ASTM D 4294 or ASTM D 4927 or ASTM D 3120
(³) ASTM D 2270

Table 2. Base oils API classification

Mineral base oils can also be classified by the production process. The most common is the solvent extraction, or conventional process, where compounds like aromatics and compounds that contain heteroatoms, as nitrogen and sulfur, are removed, increasing the VI and improving the products stability. This process also includes dewax steps, in order to reach the specified pour point, and hydrotreatment, to improve the products specifications. The non conventional process includes more severe steps of hydrocracking, where the molecules are cracked and saturated, with very stable and high VI final products.

On the other hand, synthetic base oils are produced through chemical reactions. Approximately 80% of the synthetic lubricant world market is composed by: polyalphaolefins (45%), organic esters (25%) and polyglycols (10%) (Murphy et al., 2002). The most used synthetic base oils are the polyalphaolefins, and the synthetic oils have as an

advantage, in general, higher thermal and oxidative stability, better low temperature properties and lower volatility when compared to mineral oils. However, these base oils are more expensive than mineral oils.

Applications that require high level of biodegradability need to use vegetable based synthetic base oils.

Regarding the automotive oils, the American Petroleum Institute, API, classifies the base oils in five categories as illustrated on the table 2.

The lubricant's performance is evaluated by their friction reduction, oxidation resistance, deposits formation minimization, corrosion and wear avoiding abilities. The main problem with lubricants is related to the oil degradation and its contamination by the engine combustion by-products (automotives). Thus, the main causes of engine bad working, regarding the lubricant quality, are due to deposit formation, viscosity increase, high consumption, corrosion and wear.

Deposit formation occurs when the detergent/dispersant power of the lubricant is not enough to keep the contaminants in suspension. The oil thickness results from the lubricant oxidation and the insolubles material accumulation. The viscosity increases due to the oxygenated compounds polymerization and to the insoluble products in suspension, derived from the irregular fuel burning. The sulfur level in the diesel mays cause corrosion and wear on the cylinders and rings, because of the sulfur acids or organic acids attack on the iron surfaces. To avoid this attack, lubricants with a good alkaline reserve must be used.

To minimize such problems, lubricants are obtained from the mixture between base oils and additives. These additives have antioxidant, antiwear, detergent and dispersant, and others functions. Therefore, to design a lubricant to play all these roles is a hard task which involves a careful evaluation of the base oils and additives properties.

4. Biolubricants

The world final lubricants market is about 38,000,000 tons/year (Whitby, 2005). The US market is about 9.5 millions tones, from which 32% are discarded on the environment (Lal & Carrick, 1993). On the other hand, the European biodegradable lubricants market is 172,000 tons/year, concentrated on Germany and Scandinavian countries (Whitby, 2006).

From the 1.3 million tons German lubricants market, 53% are collected as used oil, which is equivalent to 100% of all oil collection of the several applications. These used oils are recycled or used as thermal energy source. The remainder is lost to the environment as leakages, total loss applications or specific systems. Only 5% of all lubricants from the German market are biodegradable (Wagner et al., 2001). To increase this market, one must increase the acceptance and the trust on the biodegradable lubricants and decrease its price.

Nearly 13% (Europe) and 32% (USA) of all commercialized lubricants return to the environment with properties and appearance modified (Bartz, 1998). These are used on total loss wear contacts, approximately 40,000 tons/year in Germany, and on circulation systems, which are not collected neither disposed. Besides, one must take account of the lubricants from leakages and the remainder amounts in filters and recipients. Thus, the German environment is exposed to nearly 150,000 tons/year, based on the 13% previously cited. A calculation based on the current lubricants consumption in Germany and on the discard rates for the different lubricants results in nearly 250,000 tons/year. Including the not defined amount (leakages, etc.), the lubricants discarded amount on the German environment may reach 300,000 tons/year. Taking account of the lubricants market share represented by Germany, as well as the fact that in many places around the world the collect

and recycling rates of used lubricants are lower than in Europe, the total amount of lubricants returning to the environment is about 12 million tons/year.

Only 10-50% of the lubricants used on the world market are recycled (Kolwzan & Gryglewicz, 2003). The remainder, which represents millions of tons, is disposed irreversibly on the environment through leakages, oil-water emulsions, components exhaust gases, etc. Some of them are carcinogenic and resistant to biodegradation, representing a serious menace to the environment. One of the solutions to modify this situation is replacing mineral oils with biodegradable synthetic lubricants.

In the last decades, there has been an increased worldwide concern about the environmental impact from the petroleum derivatives usage. Although only approximately 1% of all consumed petroleum be used on the lubricants formulations, the most part of these products are disposed in the environment without any treatment and this concern has driven the biodegradable lubricants development.

The pollution potential of the mineral oil is extremely high. For example, 1 liter of mineral oil contaminates 1 million liters of water for the human consumption (Ravasio et al., 2002).

Regarding the 2 strokes engines (currently, the main use of biolubricants), the lubrication mechanism results in the release of unburned oil, together with exhaust gases, promoting the possibility of environmental pollution. Furthermore, when using these engines in rivers, lakes or oceans, the unburned oil, released in the water, can become a possible pollution source. Tractors, agricultural machines, chain-saws, and other forest equipments, may pollute forests and rivers, as well due to the unburned released oil.

Measures to reduce the environmental impact of lubricants, that means to eliminate or decrease the problems caused by lubricant contact, are driven by the following forces: environmental facts, public awareness, government rules, market globalization and economic incentives.

A biolubricant is a biodegradable lubricant. A substance is called biodegradable when it presents the proved capacity of being decomposed within 1 year, through natural biological processes in carbonaceous land, water and carbon dioxide (Whitby, 2005).

In general, biodegradability means a lubricant trend to be metabolized by microorganisms within 1 year. When it is complete, it means that the lubricant has essentially been back to Nature, but when it partially decomposes, one or more lubricant compounds are not biodegradable.

Some of the readily biodegradable lubricants are based on pure unmodified vegetable oils (Wagner et al., 2001), that present a biodegradability of about 99% (CEC L-33-A-93) (Birova et al., 2002). In Europe there is a predominance of sunflower and rapeseed oils, which are esters of glycerin and long chain fatty acids (triglycerides). The fatty acids are specific for each plant, being variable. The fatty acids found in natural vegetable oils differ in chain length and in their double carbon bond number. Moreover, function groups may be present. Natural triglycerides are highly biodegradable and efficient as lubricants. However, their thermal, oxidative and hydrolytic stabilities are limited. Thus, pure vegetable oils are used only on applications with low thermal requirements, as unmolding and chain-saws.

The reasons for the thermal and oxidative instabilities of the vegetable oils are the double bonds in the fatty acid molecule and the group β-CH in the alcohol counterpart (figure 3). Double bonds are especially reactive and react immediately with the air oxygen, while the hydrogen β atom is easily eliminated from the molecule structure. This results in the ester breakage in olefins and acids. A further weak point of the esters is its trend to undergo hydrolysis in the presence of water. Chemical modifications may improve the thermal,

oxidative and hydrolytic stabilities of the vegetable oils. The most important modifications occur on the carboxyl groups of the fatty acids, approximately 90%, while oleochemical reactions on the fatty acid chain are approximately 10%.
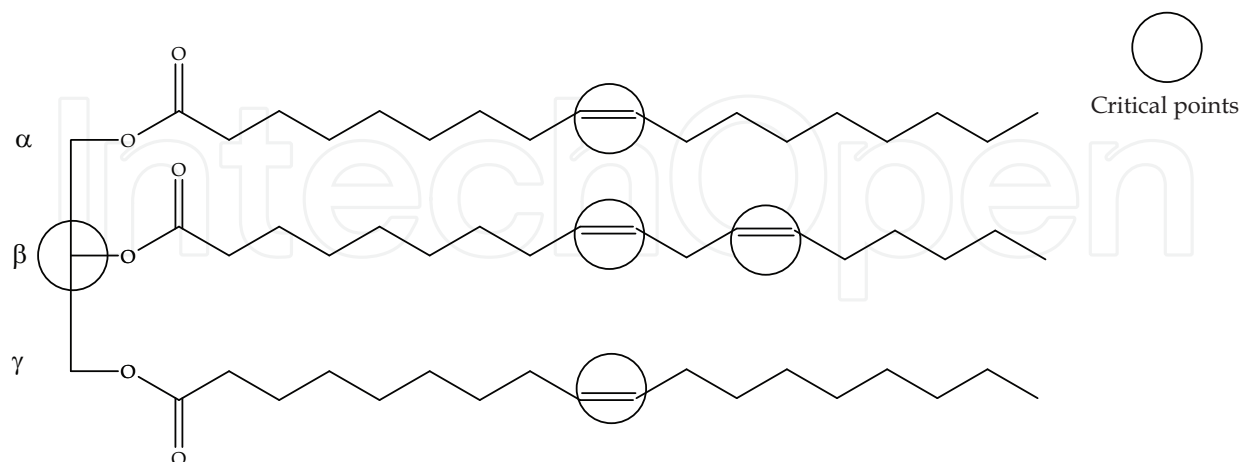

Fig. 3. Typical structure of a vegetable oil and its instability critical points

Esters, similar substances to triglycerides in terms of chemical structure, are excellent replacements for mineral oils, which possess only 20% of biodegradability (CEC-L-33-A-93). The organic esters are a growing interest in the base lubricants industry and its advantages compared to mineral base oil are (Lal & Carrick, 1993):
• Low toxicity;
• Higher biodegradability;
• Obtained from renewable sources;
• High flash point;
• Low volatility;
• High additives solvency power;
• High added value;
• Good lubricity (due to molecule polarity);
• High viscosity index (VI), due to the double bonds and the molecule linearity;
However, the main disadvantages of these compounds are:
• Oxidative instability;
• Hydrolitic instability;
• Low temperature properties.
These disadvantages can be minimized by additives, but the biodegradability, the toxicity and the price can be endangered. Thus, the chemical synthesis of these compounds seems to be the best choice to overcome these disadvantages.
The additives used traditionally are antioxidant, antiwear, anticorrosion, etc. These agents have low biodegradability. However, the additives industry has increased efforts on the development of biodegradable additives.

5. Esters

Organic esters have a wide diversity of applications in the lubricant industry because of the growing awareness of health and environment beneficial aspects, besides the benefits from better products performance: chain-saw, drilling fluids, food industry equipments,

hydraulic fluids, boat engines, 2 stroke engines, tractors, agriculture equipments, cut fluids, cooling fluids, etc (Erhan & Asadauskas, 2000).

Esters have been used as lubricants since the beginning of the 19th Century, in the form of natural esters in pig fat and whale oil (Whitby, 1998). During World War II, a large number of synthetic fluids were developed such as alcohol and long chain acids esters, that presented excellent low temperature properties.

Nowadays, the esters represent only 0.8% of the world lubricants market. However, while the global consumption of lubricants has been stagnant, the consumption of synthetic oils has grown approximately 10% per year. This growing esters consumption is due to performance reasons and also to changes on the environmental laws of several European Community countries, mainly Germany.

Esters have a low environmental impact and its metabolization consists of the following steps: ester hydrolysis, beta-oxidation of long chain hydrocarbons and oxygenases attack to aromatic nucleus. The main characteristics that reduce the microbial metabolization or degradability are:

- Branching position and degree (that reduce the beta-oxidation);
- Molecule saturation degree;
- Ester molecular weight increase.

The strongest effect of the ester group on the lubricant physical properties is a decrease in its volatility and increase in its flash point. This is due to the strong dipole moment (London forces) that keeps the ester molecules together. The ester group affects other properties, too such as: thermal and hydrolytic stabilities, solvency, lubricity and biodegradability. Besides, esters, mainly from polyalcohols, as trimethylolpropane (TMP), produce a unimolecular layer on the metal surface, protecting it against wear. This layer is produced by the oxygen atoms which are presents in the ester molecules.

The ester's most important physical-chemistry properties are viscosity, viscosity index (VI), pour point, lubricity, thermal and hydrolytic stabilities and solvency.

The main esters used as biolubricants are: diesters, phthalates, trimethilates, C_{36} dimerates and polyolesters. The polyolesters are formed from polyols with one quaternary carbon atom (neopentylalcohols), as trimethylolpropane, neopentylglycol and pentaerythritol. This class of compounds is very stable due to the absence of a secondary hydrogen on the β position and to the presence of a central quaternary carbon atom (Wagner et al., 2001). The main applications to the esters are: engine oil, 2 stroke engine oils, compressor oils, cooling fluids, aviation fluids and hydraulic fluids.

5.1 Synthesis of biolubricant esters

According to (Solomons, 1983), the carboxylic acids react with alcohols to produce esters, through a condensation reaction called esterification (figure 4). This reaction is catalyzed by acids and the equilibrium is achieved in a few hours, when an alcohol and an acid are heated under reflux with a small amount of sulfuric acid or hydrochloric acid. Since the equilibrium constant controls the amount of produced ester, an excess of the carboxylic acid or of the alcohol increases the yield of the ester. The compound choice to use in excess will depend on its availability and cost. The yield of a esterification reaction may be increased also through the removal of one of the products, the water, as it is formed.

The typical mechanism of esterification reactions is the nucleophilic substitution in acyl-carbon, as illustrated on figure 5.
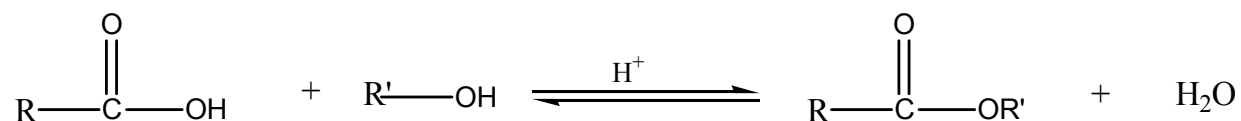
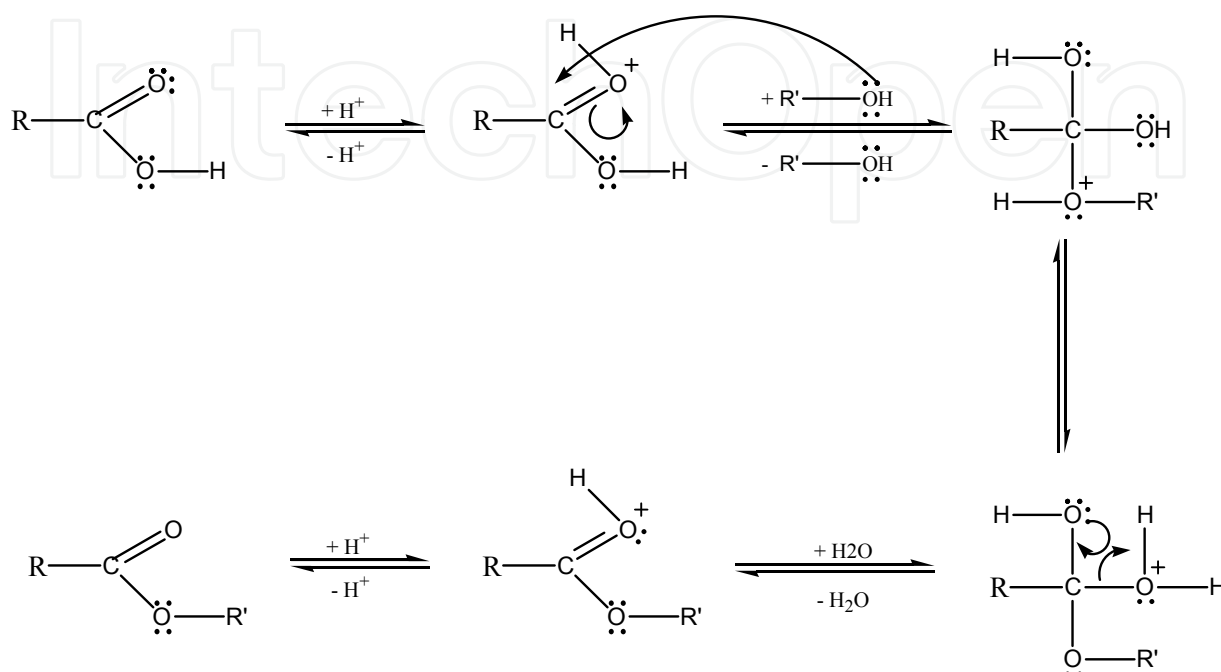Fig. 4. Esterification reaction scheme between a carboxylic acid and an alcohol

Fig. 5. Esterification reaction mechanism

When one follows the reaction clockwise, this is the direction of a carboxylic acid esterification, catalyzed by acid. If, however, one follows the counterclockwise, this is the mechanism of an ester hydrolysis, catalyzed by acid. The final result will depend on the choice conditions to the reaction. If the goal is to ersterify an acid, one uses an alcohol excess and if it is possible, one promotes the water removal as it is formed. However, if the goal is the hydrolysis, one uses a large water excess.

The steric hindrance strongly affects the reaction rates of the ester hydrolysis catalyzed by acids. The presence of large groups near to the reaction center in the alcohol component or in the acid component retards the reaction.

Esters can be synthesized through transesterification reactions (figure 6). In this process, the equilibrium is shifted towards the products, allowing the alcohol, with the lower boiling point, to be distilled from the reactant mixture. The transesterification mechanism is similar to the one of a catalyzed by acid esterification (or to the one of a catalyzed by acid ester hydrolysis).
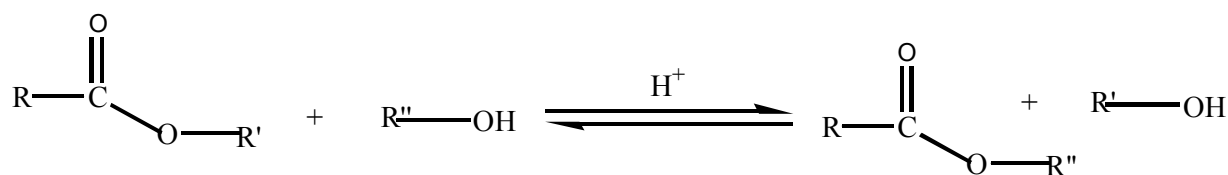

Fig. 6. Transesterification reaction between an ester and an alcohol

The methylricinoleate, from a transesterification reaction of the castor oil with methanol, is the main constituent of castor biodiesel. The transesterification of this compound with superior alcohols (TMP, Pentaerythritol or Neo-pentylglycol) (figure 7) allows the production of poliolesters, important synthetic base oils precursors.

Trimethylolpropane Ester   Pentaerythritol Ester
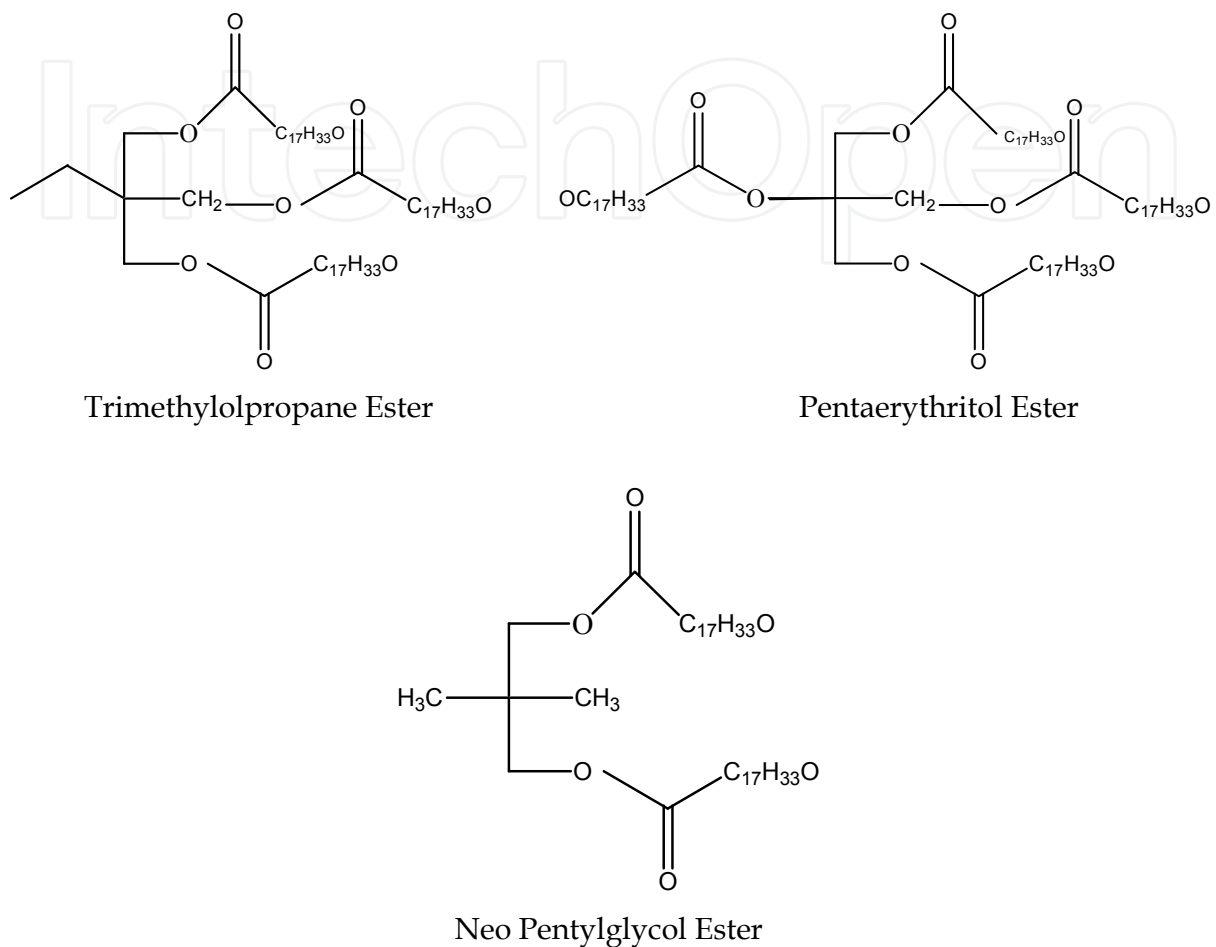
Neo Pentylglycol Ester

Fig. 7. Poliolesters molecular structures

The higher the molecule branching degree of this product the better the pour point, the higher the hydrolytic stability, the lower the VI. Regarding linearity, it is verified the opposite way. Regarding the double bonds, the higher the saturation, the better the oxidative stability, the worse the pour point (Wagner et al., 2001). Base oils from these superior alcohols, but with other vegetable oils, can be found in the market, with excellent performance.

To increase the transesterification reactions yield one must promote the reaction equilibrium shift towards the products. This can be reached by using a vacuum, which will remove the formed alcohol from the mixture.

Chemical or enzymatic catalysts may be used on the biolubricants esters synthesis. The chemical catalysis occurs in high temperatures (> 150°C), with the usage of homogeneous or heterogeneous chemical catalysts, with acid or alkaline nature (Abreu et al., 2004). The typical acid homogeneous catalysts are acid p-toluenesulfonic, phosphoric acid and sulfuric acid, while the alkaline are caustic soda, sodium ethoxide and sodium methoxide. The more popular heterogeneous catalysts are tin oxalate and cationic exchange resins.

(Bondioli et al., 2003) performed the esterification reaction between caprilic acid and TMP, using tin oxide (SnO) as catalyst at 150°C. The yield was 99%, with the continuous removal of the produced water.

(Bondioli, 2004) reported the usage of strong acid ions exchange resins as catalysts in esterification and transesterification reactions. In the case of esterification reactions, the water plays a fundamental role on the catalyst performance. If on the one hand one must remove the produced water to increase the reaction yield, on the other hand the water has a positive effect on the dissociation of the strong acid groups of the resin. Thus, a completely dry resin does not present any catalytic activity, due to the impossibility of the sulfonic group dissociation.

Another limiting factor is the reactant diffusion inside a resin. Fatty materials possess high viscosity, which limits the catalysis using ion exchange resins. In the case of a required high catalytic efficiency, one must choose ion exchange resins with a limited crosslinking degree. Powder resins are more active than spherical ones on esterification reactions.

To esters synthesis, one must to use only acid-sulfonic ion exchange resins. Strong basic ion exchange resins may be attractive for transesterification reactions, however they have a limited stability when heated at temperatures higher than 40°C, and are neutralized by low concentrations of fatty acids. Another negative factor is the glycerin production during the reaction, which can make the resin waterproof.

In spite of these negative effects, ion exchange resins, when used as heterogeneous catalysts, present the following operational advantages:

- As solid acids or bases, in a batch process, they can easily be separated from the system at the reaction end;
- One may prepare the catalytic bed by packaging and produce a continuous process with higher productivity and catalytic efficiency;
- The possibility of regeneration decreases the process costs;
- Due to its molecular sieve action, there is a higher selectivity;
- These resins are less corrosive than the regular used acids and bases.

Biolubricants esters synthesis may be performed with efficiency using not only chemical catalysts but also biological ones (lipases). However, catalyst choice parameters must be based on the knowledge of each one's limitation. Thus, although the chemical via presents a main advantage because of the lower cost when compared to the enzymatic via, due to its higher availability in large amounts, it also presents some disadvantages, such as:

- Low catalyst selectivity, with several parallel reactions;
- Corrosion, mainly with sulfuric acid and sodium hydroxide as catalysts;
- Low conversion (40% in average), mainly with metal complex catalysts;
- Foam production (Basic catalysts);
- Almost any catalytic activity (H_2SO_4 and NaOH) with long chain alcohols;
- More severe operation conditions and higher energy consumption due to higher temperatures required.

Regarding the enzymatic catalysis, it occurs in milder temperatures (60°C), using lipases, triacyl ester hydrolases (glycerol ester hydrolases, E.C. 3.1.1.3). Normally, the lipases catalyze the glycerol ester hydrolysis in lipid/water interphases (Dossat et al., 2002). However, in aqua restrict systems, for example, solvents, lipases catalyze also the synthesis of such esters. Thus, they have been employed on the fat and oil modifications, in aqua restrict systems with or without the presence of organic solvents. Lipases from several

microorganisms have been studied in the vegetable oil transesterification reactions, such as: *Candida rugosa, Chromobacterium viscosum, Rhizomucor miehei, Pseudomonas fluorescens* and *Candida antarctica*. The most used among these are *Rhizomucor miehei* (immobilized in macroporous anionic resin – Lipozyme) and *Candida rugosa*, in powder. In works made with sunflower oil, the *Candida rugosa* lipase usage showed a higher yield in the transesterification reaction, besides a lower cost than the *Rhizomucor miehei* lipase (Castro et al., 2004).

The transesterification reactions via enzymes may occur with or without the presence of organic solvents. Other interesting variable on this type of reactions is the added amount of alcohol. A large alcohol excess shifts the reaction equilibrium to the production of ester. However, literature data show that a very large excess (higher than 1:6, ester:alcohol) can cause inhibition of the enzymatic activity.

Another interesting characteristic regarding these reactions can be seen in transesterifications directly from the vegetable oils. These reactions have glycerin as subproduct, which, according to some authors, may be adsorbed on the enzyme surface, thus inactivating it (Dossat et al., 2002).

The enzymatic via shows some advantages, as well for example:

• High enzyme selectivity;
• High yields on the ester conversion;
• Milder reaction conditions, avoiding degradation of reactants and products;
• Lower energy consumption, due to low temperatures;
• Catalyst biodegradability;
• Easy recover of the enzymatic catalyst (Dossat et al., 2002).

A main disadvantage of this via is the high cost of the industrial scale process, due to the high cost of the enzymes. However, the development of more robust biocatalysts through molecular biology techniques or enzymes immobilization can make this process more industrially competitive in a few years.

The biolubricants esters synthesis can be carried out not only in batch reactors, but also in continuous reactors (fixed or fluidized bed). However, due to process simplicity, the batch is the majority choice. One illustrative example of a batch reactor is on figure 8.

(Lämsa, 1995) studied and developed new methods and processes regarding the esters production from vegetable oils, raw-materials for the biodegradable lubricants production, using not only chemical catalysts but also enzymatic catalysts. On the beginning it was synthesized 2-ethyl-1-hexyester of rapeseed oil, from 2-ethyl-1-hexanol and rapeseed oil, ranging catalysts (sodium hydroxide, potassium hydroxide, sodium methoxide, sodium ethoxide and sulfuric acid), molar ratio oil:alcohol (1:3 to 1:6), temperature (80 to 120°C) and pressure (2.0 to 10.6 MPa).

The established optimum conditions were: molar ratio (1:5), 0.5% alkaline catalyst (sodium methoxide), temperature range 80 to 105°C and pressure of 2.7 MPa. The obtained rapeseed yield was 97.6% in five hours of reaction.

The above described synthesis was also studied using *Candida rugosa* lipase as catalyst, with a yield of 87% in five hours of reaction. The best conditions were: molar ratio oil:alcohol (1:2.8), lipase concentration (3.4%), added water (1.0%) and temperature of 37°C.

(Lämsa, 1995) synthesized also a rapeseed methyl ester (biodiesel), reacting rapeseed with methanol (in excess) at 60°C, using 0.5% of alkaline catalyst. After four hours of reaction, the yield was 97%, with the separation of the formed glycerin and the distillation of the excess alcohol.

Fig. 8. Transesterification batch reactor

The same author still promoted the reaction between the rapeseed methyl ester and trimethylolpropane (TMP). This transesterification reaction followed a strategy of individual analyses of each variable behavior involved in the process. Firstly, it was studied the type and the amount of catalyst used, with the best results attributed to sodium methoxide (0.7%). Next, the molar ratio ester:TMP was evaluated, with the best value being 3.2:1 (small ester excess). Finally, the temperature and the pressure were studied, both of these variables have a strong effect on the yield. It was established the values of 85-110°C and 3.3 MPa for a yield of 98.9%, in 2.5 hours of reaction.

At last, the author performed the rapeseed methyl ester synthesis through enzymatic catalysis. The yields using lipases were high, but the reaction duration was extremely high (46 hours in average).

6. Biolubrificant properties

The main properties of a lubricant oil, which are basic requirements to the good performance of it, will be described as follows:

a. Viscosity: the viscosity of lubricants is the most important property of these fluids, due to it being directly related to the film formation that protects the metal surfaces from several attacks. In essence, the fluid viscosity is its resistance to the flow, which is a function of the required force to occur slide between its molecule internal layers. For the biolubricants, there is not a pre-defined value, however, due to market reasons, the range 8 to 15 cSt at 100°C is the most required;

b. Viscosity index (VI): it is an arbitrary dimensionless number used to characterize the range of the kinematic viscosity of a petroleum product with the temperature. A higher viscosity index means a low viscosity decrease when it increases the temperature of a product. Normally, the viscosity index value is determined through calculation (ASTM D2270 method), which takes in account the product viscosities at 40 and 100°C. Oils with VI values higher than 130 find a wide diversity of applications;

c. Pour point: this essay was for a long period of time the only one used to evaluate the lubricants behavior at low temperatures. After pre-heating, the sample is cooled at a specified rate and observed in 3°C intervals to evaluate the flow characteristics. The lowest temperature where is observed movement in the oil is reported as the pour point. The lower the pour point, the better the base oil, having values lower than -36°C a wide market. Some pour point depressants may be used on the biolubricants formulations, but these are less efficient than when used with mineral oils;

d. Corrosion: biolubricants, as mineral lubricants, must not be corrosives. Because of that, they must present 1B result (maximum) on the test ASTM D130, which consists on the observation of the corrosion in a copper plate after this plate is taken out from an oven, where it has been for 3 hours, immersed in the lubricant sample, at 150°C. The values 1A, 1B, etc., are attributed based on comparison with standards;

e. Total acid number (TAN): this essay's goal is to measure the acidity of the lubricant, derived, in general, from the oxidation process, the fuel burning and some additives. In this essay, a sample, with known mass, is previously mixed with titration solvent and titrated in KOH in alcohol. It is determined the KOH mass by sample mass to the titration. It is desired values lower than 0.5 mgKOH/g, since higher TAN values contribute to increase the corrosion effects;

f. Biodegradability: many vegetable oils and synthetic esters are inherently biodegradable. This means that they are not permanent and undergo physical and chemical changes as a result of its reaction with the biota, which leads to the removal of not favorable environmental characteristics. The negative characteristics are water immiscibility, eco toxicity, bioaccumulation in live organisms and biocide action against such organisms. For some applications, the lubricants must be readily biodegradable. The tests CEC L-33-T-82 and modified STURM are two of the most widely used to measure the lubricants biodegradability. To consider a lubricant as biodegradable, for example, it must present a result higher than 67% on the CEC test;

g. Oxidative stability: most parts of the vegetable oils are unsaturated and trend to be less stable to oxidation than mineral oils. Low amounts of antioxidants (0.1-0.2%) are effective in mineral oil formulations. However, vegetable oils may require a large amount of such antioxidants (1-5%) to prevent its oxidative degradation. The most used essay to measure the oxidative stability of lubricants is the Rotary Pressure Vessel (RPVOT – ASTM D2272). A good lubricant must present an oxidation times higher than 180 minutes, on this method.

7. Conclusion

The biolubricants market has increased at an approximately 10% per year rate in the last ten years (Erhan et al., 2008). The driven forces of such increase are mainly the growing awareness regarding environmental friendly products and government incentives and regulations.

Even though, when compared to the mineral oil market, the biolubricants usage is very small, and, as mentioned before, concentrated in some countries of Europe and in the USA. In order to change the scenario, the biggest challenge to the industries is how to reduce the production costs of such products, therefore making its prices more attractive. The chemical process has low costs, but the yields are a little small. On the other hand, the enzymatic process, with high yields, possesses elevated costs. The newest technologies in lipases development and immobilization may contribute to decrease these costs and make these products cheaper.

Another important matter related to the biolubricants is the quality of their characteristics. On properties as viscosity, viscosity index and pour point, these products overcome the mineral oils based lubricants. But in terms of oxidative stability, efforts have been made to develop products with at least the same level of mineral oils. This can be achieved by chemical modification, acting on the biolubricant molecule, or by adding some special developed additives. The problem is that these additives must be biodegradable too, in order to not damage the biodegradability of the product as a whole. The additives and the lubricants industries have worked together towards the development of environmental friendly products.

The usage of each country's typical raw materials, like castor oil in Brazil, is used both for an economic reason and a social reason. In the Brazilian case, the small farmers of the poorest country regions are encouraged to plant castor, which is a very easily cultivated crop due to the Brazilian weather. They are able to sell these castor seeds for the oil and biodiesel producers, who can then produce biolubricants. This is a very interesting way to promote the social inclusion in underdeveloped countries. And another interesting feature of this crop is that there is not any food competition.

Finally, the biolubricants have a very important role in the future of mankind, because their potential to contribute to an environment free of pollution and with more equal opportunities for the entire World.

8. References

Abreu, F. R.; Lima, D. G.; Hamú, E. H.; Wolf C. & Suarez, P. A. Z. (2004). Utilization of Metal Complexes as Catalysts in the Transesterification of Brazilian Vegetable Oils with Different Alcohols. *Journal of Molecular Catalysis A: Chemical*, Vol. 209, pp. 29-33.

Azevedo, D. M. P. & Lima, E. F. (2001). *O Agronegócio da Mamona no Brasil*, Embrapa, (21st edition)., Brasília, Brazil.

Bartz, W. J. (1998). Lubricant and the Environment. *Tribology International*, Vol. 31, pp. 35-47.

Birová, A.; Pavlovicová, A. & Cvengros, J. (2002). Lubricating Oils Base from Chemically Modified Vegetable Oils. *Journal of Synthetic Lubrication*, Vol. 18, No. 18-4, pp. 292-299.

Bondioli, P.; Della Bella, L. & Manglaviti, A. (2003). Synthesis of Biolubricants with High Viscosity and High Oxidation Stability. *OCL*, Vol. 10, pp. 150-154.

Bondioli, P. (2004). The Preparation of Fatty Acid Esters by Means of Catalytic Reactions. *Topics in Catalysis*, Vol .27, No. 1-4 (Feb), pp. 77-81.

Castro, H. F.; Mendes, A. A.; Santos, J. C. & Aguiar, C. L. (2004). Modificação de Óleos e Gorduras por Biotransformação. *Química Nova*, Vol. 27, No. 1, pp. 146-156.

Dossat, V.; Combes, D. & Marty, A. (2002). Lipase-Catalysed Transesterification of High Oleic Sunflower Oil. *Enzyme and Microbial Technology*, Vol. 30, pp. 90-94.

Erhan, S. Z. & Asadauskas, S. (2000). Lubricant Basestocks from Vegetable Oils. *Industrial Crops and Products*, Vol. 11, pp. 277-282.

Erhan, S. Z., Sharma, B. K., Liu, Z., Adhvaryu A. (2008). Lubricant Base Stock Potential of Chemically Modified Vegetable Oils. *J. Agric. Food Chem.*, Vol. 56, pp. 8919-8925.

Kolwzan, B. & Gryglewicz, S. (2003). Synthesis and Biodegradability of Some Adipic and Sebacic Esters. *Journal of Synthetic Lubrication*, Vol. 20, No. 20-2, pp. 99-107.

Lal, K. & Carrick, V. (1993). Performance Testing of Lubricants Based on High Oleic Vegetable Oils. *Journal of Synthetic Lubrication*, No. 11-3, pp. 189-206.

Lämsa, M. (1995). *Environmentally Friendly Products Based on Vegetable Oils*. D.Sc. Thesis, Helsinki University of Technology, Helsinki, Finland.

Lastres, L. F. M. (2003). *Lubrificantes e Lubrificação em Motores de Combustão Interna.* Petrobras/CENPES/LPE, Rio de Janeiro, Brazil.

Murphy, W. R.; Blain, D. A. & Galiano-Roth, A. S. (2002). Benefits of Synthetic Lubricants in Industrial Applications. *J. Synthetic Lubrication*, Vol. 18, No. 18-4 (Jan), pp. 301-325.

Ravasio, N.; Zaccheria, F.; Gargano, M.; Recchia, S.; Fusi, A.; Poli, N. & Psaro, R. (2002). Environmental Friendly Lubricants Through Selective Hydrogenation of Rapeseed Oil over Supported Copper Catalysts. *App. Cat. A: Gen.*, Vol. 233, pp. 1-6.

Solomons, T. W. G. (1983). *Química Orgânica*, LTC, (1st edition), Rio de Janeiro, Brazil.

Wagner, H.; Luther, R. & Mang, T. (2001). Lubricant Base Fluids Based on Renewable Raw Materials. Their Catalytic Manufacture and Modification. *Applied Catalysis A: General*, Vol. 221, pp. 429-442.

Whitby, R. D. (1998). Synthetic and VHVI-Based Lubricants Applications, Markets and Price-Performance Competition. Course Notes, Rio de Janeiro, Brazil.

Whitby, R. D. (2005). Understanding the Global Lubricants Business – Regional Markets, Economic Issues and Profitability. Course Notes, Oxford, England.

Whitby, R. D. (2006). Bio-Lubricants: Applications and Prospects. In: *Proceedings of the 15th International Colloquium Tribology*, Vol. 1, pp. 150, Ostfildern, Germany, January, 2006.
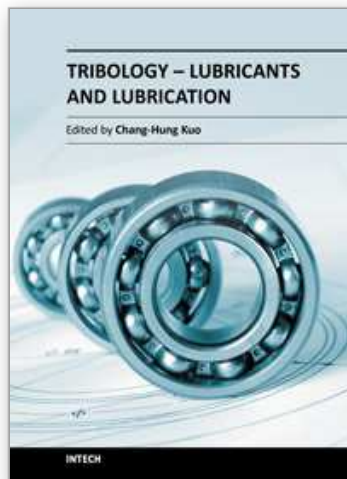
Tribology - Lubricants and Lubrication

Edited by Dr. Chang-Hung Kuo

In the past decades, significant advances in tribology have been made as engineers strive to develop more reliable and high performance products. The advancements are mainly driven by the evolution of computational techniques and experimental characterization that leads to a thorough understanding of tribological process on both macro- and microscales. The purpose of this book is to present recent progress of researchers on the hydrodynamic lubrication analysis and the lubrication tests for biodegradable lubricants.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

José André Cavalcanti da Silva (2011). Biodegradable Lubricants and Their Production Via Chemical Catalysis, Tribology - Lubricants and Lubrication, Dr. Chang-Hung Kuo (Ed.), ISBN: 978-953-307-371-2, InTech, Available from: http://www.intechopen.com/books/tribology-lubricants-and-lubrication/biodegradable-lubricants-and-their-production-via-chemical-catalysis

INTECH

open science | open minds