Elsevier Editorial System(tm) for Tribology International
Manuscript Draft

Manuscript Number: TRIBINT-D-16-01015R2

Title: TRIBOLOGICAL CHARACTERIZATION OF VEGETAL LUBRICANTS: COMPARATIVE EXPERIMENTAL INVESTIGATION ON JATROPHA CURCAS L. OIL, RAPESEED METHYL ESTER OIL, HYDROTREATED RAPESEED OIL

Article Type: Full Length Article

Keywords: Vegetal Lubricants; Tribology; Physicochemical Properties; Friction Coefficient

Corresponding Author: Dr. Roberto D'Amato, Ph.D.

Corresponding Author's Institution: Universidad Politécnica de Madrid

First Author: Alessandro Ruggiero, Professor

Order of Authors: Alessandro Ruggiero, Professor; Roberto D'Amato, Ph.D.; Massimiliano Merola; Petr Valášek, Professor; Miroslav Müller, Professor

Abstract: In this work the physicochemical and the tribological performances of three plant seed based oils in the lubricating contact pair AISI E52100 steel sliding against X210Cr12 steel are investigated. Fatty Acid Methyl Ester, Hydro Treated Vegetable oils from raw rapeseed oil and raw Jatropha Curcas L. oil(JCLO)were chosen. The tribo-tests were carried out using ball-on-flat reciprocatory tribometer for several frequencies and normal loads for 30 minutes. The oils exhibited good physicochemical properties and could be favourably used as lubricant feedstock in industrial application. The friction coefficient in all tests, for the HVO, stays in the range of 0.114-0.164, in the range of 0.114-0.164 for the RME and in the range of 0.095-0.119 for the JCLO.

Cover Letter

Madrid, 04.08. 2016

Editor-in-Chief
Tribology international, Elsevier

Dear Mr. Fillon:

Enclosed for your consideration is our original research paper:

" *TRIBOLOGICAL CHARACTERIZATION OF VEGETAL LUBRICANTS: COMPARATIVE EXPERIMENTAL INVESTIGATION ON JATROPHA CURCAS L. OIL, RAPESEED METHYL ESTER OIL, HYDRO-TREATED RAPESEED OIL”*

By Prof. Alessandro Ruggiero, PhD Roberto D'Amato, MEROLA Massimiliano, Prof. Valašek Petr, Prof. Müller Miroslav.

We confirm that all authors were fully involved in the study and preparation of the manuscript.

The content of this manuscript have not been copyrighted or published previously, nor is now under consideration for publication elsewhere.

Linked with our former and ongoing research, the physicochemical and tribological performances of three plant seed based oils in the lubricating contact pair AISI E52100 steel sliding against X210Cr12 steel are investigated . Fatty Acid Methyl Ester, Hydro Treated Vegetable oils from raw rapeseed oil and raw Jatropha Curcas L. oil were chosen. The tests were carried out by using a reciprocating tribometer in dry and lubricated conditions. The CoF was measured with several loads and several frequencies.

The proposed methodology and calculation possibilities are foreseen as a potential contribution to studies of the tribological properties of the based plant oil in relationship with lubrication.

We thank you in advance for the attention paid to our paper which would hopefully be of interest to the readers of the Tribology International.

Yours sincerely,

Dr. Eng. Roberto D’Amato
Departamento de Ingeniería Mecánica, Química y Diseño Industrial,
Universidad Politécnica de Madrid.
Ronda de Valencia, 3 – 28012 Madrid, Spain
Tel.: + 0034 913365585
r.damato@upm.es

Statement of Originality

Linked with our former though still ongoing research, in this work the physicochemical and tribological performances of three plant seed based oils in the lubricating contact pair AISI E52100 steel sliding against X210Cr12 steel are investigated. The tribo-tests were carried out using ball-on-flat reciprocatory tribometer for several frequencies and normal loads. The friction coefficient was measured with several loads and several frequencies to investigate on the tribological behaviour of the couplings. Fatty Acid Methyl Ester, Hydro Treated Vegetable oils from raw rapeseed oil and raw Jatropha Curcas L. oil were chosen. The oils were analyzed for their chemical and physical properties such as viscosity, density flash point and TAN.The results were interpreted on the basis of the evolution of the friction coefficient in order to understand the lubrication mechanisms. The novelty of the proposed methodology and calculation possibilities resides in a contribution to studies the physicochemical and the tribological properties of the Plant-based oils in a steel contact.

Highlights

- Experimental analysis of tribological behaviour of AISI E52100 steel sliding against X210Cr12 steel;
- Physicochemical and tribological performances of three plant seed based oils in the lubricating contact;
- Fatty Acid Methyl Ester, Hydro Treated Vegetable oils from raw rapeseed oil and raw Jatropha Curcas L. oil were chosen;
- We used a reciprocating tribometer in dry and lubricated conditions ;
- The CoF, chemical and physical properties such as viscosity, density flash point and TAN were measured;

The Authors are grateful to the reviewer whose helpful comments allowed an improvement of the paper. The paper was corrected on the basis of these suggestions.
Corrections are reported along the manuscript highlighted in yellow.

Reviewer #3: The manuscript have been improved, but I still miss a clear thread to point out the scientific aims and originality of this manuscript. The number of results are quiet interesting but authors do no achieve a suitable discussion of these results. I found that the new discussion of the results in relation with adhesion phenomena is speculative and not well supported. In relation with my review, I still detecting some un-resolved comments and need significant improvements in relation with.

It is well know that fatty acid composition affect the tribological behaviour of vegetable oil-based lubricant. Authors used three different vegetable oils but no comment about the significant influence of the fatty acid composition is made.

The authors have added in section 2.1 the fatty acids composition for JCL oil and RME oil. The authors in the same section, as described in the introduction, have reported the alkenes composition of HVO oil. In fact, Chemically hydrotreated vegetable oil (HVO) is mixtures of paraffinic hydrocarbons and is free of sulfur and aromatics. In the conclusions furthermore, as request by the Reviewer, the Authors have added a discussion on the influence of the fatty acid composition on tribological performances.

The rheological results showed in Figure 5 should be plotted in log-log scale. In addition to this, the geometry (cone-plate, plate-plate or coquette geometries) used for these steady state test should be mention in section 2.2. I am not sure that results are not affected by expulsion problems or wall-depletion phenomena.

The Authors have tried to change Figure 5 as suggested by the reviewer, but the graph appears to be not clear and its understanding is not easy. It is opinion of the Authors that it is better to keep the Figure 5 as it is. Others examples of the used representation (no log-log scale) are reported in referenced literature:
R.A. Candeia, M.C.D. Silva, J.R. Carvalho Filho, M.G.A. Brasilino, T.C. Bicudo, I.M.G. Santos, A.G. Souza, *Influence of soybean biodiesel content on basic properties of biodiesel–diesel blends*, Fuel. 88 (2009) 738–743.
M. Kargulewicz, I. Iordanoff, V. Marrero, J. Tichy, *Modeling of Magnetorheological Fluids by the Discrete Element Method*, J. Tribol. 134 (2012) 31706. doi:10.1115/1.4006021.

About the Reviewer perplexity on the used test methods, it is well known that in order to evaluate the rheology properties of any kind of fluid it is possible to use four kind of rotational rheometers (cone-plate, plate-plate, coquette and Brookfield viscometers) [Faith Morrison, “Understanding Rheology,” Oxford University Press (2001)
Malkin, A.Y. & A.I. Isayev, “Rheology: Concepts, Methods & Applications,” ChemTec Publishing, Toronto (2006).
H. A. Barnes “A Handbook of Elementary Rheology”, University of Wales, Institute of Non-Newtonian Fluid Mechanics, 2000].
In our work we used a Dial Brookfield RV Viscometer; in the revised version of the manuscript this information was reported in section 2.2 (Physicochemical Properties of the oils): “A deal reading RV Brookfield Viscometer was used to evaluate the behaviour of the dynamic viscosity”.
In order to clarify and to give more information about, the Authors improved this sentence in the manuscript as follows:
“In order to evaluate the behavior of the dynamic viscosity a verified Dial Brookfield

(Viscometer RV) rotational type was used. The Dial Brookfield Viscometer (accuracy ±1% and repeatability ±0.2%) is equipped with a guard leg and a spindle series under Brookfield Society Engineering recommendation."
Furthermore, this set-up allows to avoid expulsion problem and wall-depletion phenomena (see reference H. A. Barnes 2000 (pages 42-44), cited above).

The physicochemical analysis of the three oils is not well linked with the aims of this work. In fact, it has been previously pointed out that both transesterification and hydrotreatment of vegetable oils produce not bad physicochemical properties for lubrication. Moreover, the discussion of these physicochemical properties (density, flash point and TAN) is still missed in the results and discussion section, although it appears in the conclusion section. It seems to be no relevant for these comparative tribological characterization, which is the main objective of this experimental work. Therefore, authors should connect the physicochemical analysis with tribological characterization and discuss conveniently in the results and discussion section.

Discussion on the physicochemical properties was added in Section 3: *Results and Discussion* as suggested by the reviewer. And the connection of these properties with the tribological ones was made.

In relation with new statements, how can authors explain that HVO produced the lowest wear volume if this oil has the highest CoF and low viscosity? Please, take into account that in both cases the lubrication regimen (Stribeck's curve) is the same. The current discussion is not well defended and supported.

Regarding the observation of the reviewer, the Authors believe that the possible solution to this concern is more likely linked to the formation of oxides at the interface coupling (in Figure 8 it is possible to see how the surface of the worn spheres is darker than the other cases, i.e. presence of oxide substrates). This phenomenon is most likely due to the higher temperature reached (standing the same kinematic parameters of the other oils) as consequence of a higher friction coefficient. With regards to reference [Azman, Nurul Farhanah, and Syahrullail Samion. "*Improvement of Lubrication Performance of RBD Palm Stearin as Alternative Lubricant under Different Sliding Speeds*." Strojniški vestnik - Journal of Mechanical Engineering (2015)] it is declared that:
"Wear debris will form during abrasion, where oxidation of the debris will eventually raise the COF [Autay, R., Kchaou, M., Dammak, F. (2012). Friction and wear behavior of steels under different reciprocating sliding conditions. *Tribology Transactions, vol. 55, no. 5, p. 590–598]. However, a rise in temperature will cause the formation of an oxide layer. It was observed in some previous researches that this oxide film offers a certain amount of protection from wear [Gunes, I., Uygunoglu, T. and Erdogan, M. (2015).* Effect of sintering duration on some properties of pure magnesium. *Powder Metallurgy and Metal Ceramics, vol. 54, no. 3–4, pp. 156–165. Syahrullail, S. and Ismail, M.S.J. (2013).* Lubrication performance of double fraction palm olein using pin-on-disk tribotester*. IOP Conference Series: Materials Science and Engineering, vol. 50, p. 012002]".*
The Authors assert, as also reported in [Azman and Samion 2015 (cited above)], that this phenomenon needs appropriate investigations aimed also to the thermal and oxidative analysis of the tribo-couple, which was not carried on in this work. Therefore, not having these results, the Authors prefer not to include a discussion on this aspect.
Furthermore, as reported in the manuscript: "It can be explained through the presence of low quantity of Palmitic acid and stereatic acid. In fact, the anti-wear behaviour of fatty acids is the result of complex interactions between molecules of the acid and particular

types of hydrocarbons [69]”.
However the above considerations, with related references, on this topic were added in the manuscript.

Conclusion section need to be rewritten with only the new contributions to the tribological behaviour of these vegetable oil-based lubricants.

The Conclusion Section was rewritten with only the new contributions to the tribological behavior.

TRIBOLOGICAL CHARACTERIZATION OF VEGETAL LUBRICANTS: COMPARATIVE EXPERIMENTAL INVESTIGATION ON JATROPHA CURCAS L. OIL, RAPESEED METHYL ESTER OIL, HYDROTREATED RAPESEED OIL

Authors:

RUGGIERO Alessandro - Department of Industrial Engineering, University of Salerno, Italy

D'AMATO Roberto - Departamento de Ingeniería Mecánica, Química y Diseño Industrial, Universidad Politécnica de Madrid. Spain –

MEROLA Massimiliano - Department of Industrial Engineering, University of Salerno. Italy

VALAŠEK Petr - Czech University of Life Sciences Prague, Faculty of Engineering, Department of Material Science and Manufacturing Technology, Prague, Czech Republic

MÜLLER Miroslav - Czech University of Life Sciences Prague, Faculty of Engineering, Department of Material Science and Manufacturing Technology, Prague, Czech Republic

Keywords: Vegetal Lubricants; Tribology; Physicochemical Properties; Rheology; Friction Coefficient; Experimental;

Corresponding author: D'AMATO Roberto

Mailing address: Ronda de Valencia, 3, 28012 Madrid

Email address: r.damato@upm.es

Abstract

Biodegradability, good lubricating properties and low production costs, are the reasons to consider the plant oils a good alternative as reference to replace the petroleum-based oils that have limited resources. The based plant oils are very attractive as alternative lubricant source. Therefore, the aim of this work is to investigate on physicochemical and tribological performances of three plant seed based oils in the lubricating contact pair AISI E52100 steel sliding against X210Cr12 steel. Fatty Acid Methyl Ester (FAME), Hydrotreated Vegetable oil (HVO) from raw rapeseed oil and raw Jatropha Curcas L. oil (JCL) were chosen. The oils were analysed for their chemical and physical properties such as viscosity, density flash point and TAN. The tribo-tests were carried out using ball-on-flat reciprocatory tribometer for several frequencies and normal loads. The oils exhibited good physicochemical properties and could be favourably used as lubricant feedstock in industrial application. The friction coefficient in all tests, for the HVO, stays in the range of 0.14-0.17, in the range of 0.11-0.14 for the Rapeseed Methyl Ester oil (RME) and in the range of 0.11-0.13 for the Jatropha Curcas L. seed oil. JCL showed the lowest CoF among the three oils examined, followed by RME and HVO. Whereas, spheres lubricated with HVO underwent to the lowest wear but presented the highest roughness.

Introduction

Growing environmental concerns provide motivation to increase the demand and use of environmentally friendly fluids [1] in various industrial sectors such as agriculture, sailing and the railway industry [2]. Over the last few years, the research for manufacturing new products and the development of sustainable green chemistry makes the plant oils attractive for lubricating purpose. Numerous fluids used as lubricants are mineral oil-based and they are obtained primarily from petroleum derivatives and, subsequently, used in automotive transmission fluids, neat cutting oils, hydraulic fluids, industrial gear oils, cold rolling oils and automotive gear lubricants [3]. Unfortunately, due to their low biodegradability and high toxicity, these oils are not a viable alternative. Furthermore, due to the poor availability of petroleum, to the involvement of Petroleum crude oils in many political situations and its high cost, the alternative energy sources are having an increasingly important role in industry. Thanks to several advantages, such as low environmental pollution, easy additive combinations [4], biodegradability [5,6], low production costs [7], low toxicity, high flash points, low volatility and high viscosity indices [2], the plant oils represent a good alternative to petroleum oils. Due to environmental and economic reasons, the plant oils, recycled waste or used oils after their appropriate chemical modification [8], are used for industrial purposes, specifically as lubricants. For these reasons and for their excellent lubricity, the oil-based lubricants and their derivatives are being investigated as a base stock for lubricants and functional fluids [9]. Most of the raw materials for the preparation of vegetable oils are originated from oleaginous plants: sunflower, soybean, rape seed, cotton and, in the tropical zone, from palms, coconut tree, jatropha curcas l [8,10]. For example, in American companies the most produced oil in large scale is soybean oil [8]. In Europe, the cheapest and most popular oil is rapeseed oil [10,11]. The use of vegetable oils as lubricants under boundary and hydrodynamic lubrication regime is corroborated by their chemical structure with long fatty acid chains [12]. Plant oils have greater anticorrosion properties for metal surface and higher viscosity indices. However, the vegetable oils tend to show low oxidative stability and higher melting points. In order to solve this kind of disadvantages the vegetable oils are subjected to chemical modifications with independent approaches [13–15]. All crude plant oils, from a chemical point of view, have a triacylglycerol structure and are chemically composed of saturated and unsaturated fatty acids triglycerides. The presence of $C=C$ unsaturated bonds is normally the cause for poor oxidative stability. One of the most important and cheapest methods to improve the viscosity index and thermo oxidative stability is the transesterification [16]. The preparation of esters of lower alcohols and fatty acids of vegetable oils through the transesterification process involves the reaction oil with ethyl alcohol or methyl alcohol using homogeneous catalysts. The catalyst can be KOH, $NaOH$, or H_2SO_4 [17,18] and the reaction also produces the glycerol (**Figure 1**).

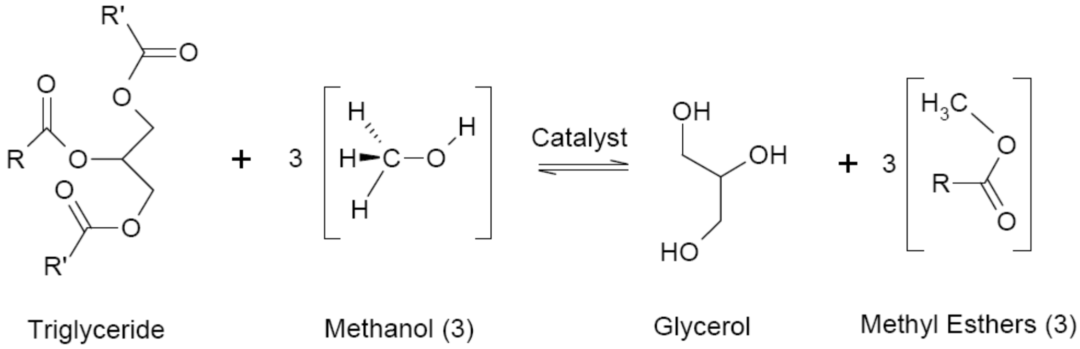

Figure 1: Transesterification reaction

After the esterification of rapeseed oil other processes are needed: separation of esterification products, methanol distillation and purification of the ester. The product obtained, called FAME (Fatty Acid Methyl Ester) that means methyl ester of the higher fatty acids found in raw plant oil, after the transesterification process is also used as fuel oil additives or in the pure form as the “Biodiesel”.

Another chemical modification to improve the lubricity and the stability of the raw plant oil is the Hydrotreated or Hydrogenation. From a chemical point of view, Hydrotreated Vegetable Oil (HVO) is a mixture of paraffinic hydrocarbons and the chemical structure is C_nH_{2n+2} [19]. The process uses the hydrogen to remove the oxygen and also to eliminate possible unsaturations, converted in water, from the triglyceride and paraffins. The process to produce HVO, with respect to the transesterification (FAME), does not need additional chemicals (Methanol) and does not produce glycerol as a side product of the reaction [20]. The mechanism of the reaction to produce HVO consists of a series of consecutive steps (**Figure 2**) such as hydrodeoxygenation, decarboxylation, and decarbonylation [21].

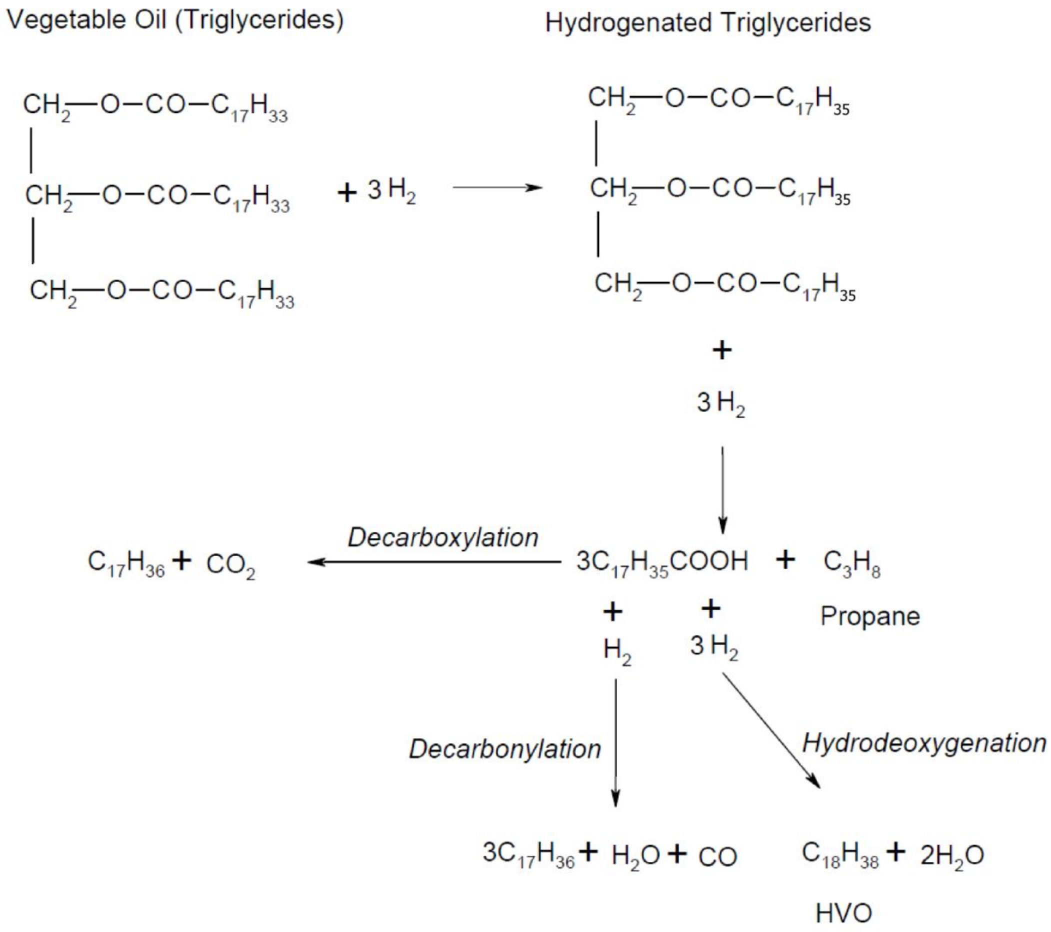

Figure 2: An example of Hydrotreated to obtain HVO

The process involves the formation of propane as a byproduct which can be used for the production of energy or in chemical synthesis.

Due to their good lubricating and protective (anti-corrosive) properties [22,23] the raw rapeseed oil and Jatropha Curcas L. oil are two of the most common sources for environmentally friendly lubricant. It is important to note that the rape seed oil and Jatropha oil have a low level of toxicity and a great degree of biodegradability along with the above-mentioned properties. The results of the work by [24] indicate that in highly loaded contacts, i.e., under elastohydrodynamic regime, rapeseed oil would provide the lowest shear stress on the sliding surfaces, about 70% of the value of a naphthenic oil. This will cut friction losses and so increase efficiency. Rapeseed oil has the benefit of both producing a relatively thick protective oil film and giving relatively low friction [24]. Recently, many study have been done on wear properties of vegetable oil using different tribometer techniques. Sulek et al. [25] investigated the tribological properties of rapeseed methyl ester oil by HFRR tribometer. Haseeb et al. in their four-ball wear test on the tribological properties of the Palm methyl ester oil found that the friction and wear increase with increasing temperature [26]. In several study the result on the tribological performance show that the vegetable oil outperformed mineral base oils in antiwear and friction [27] and [28] and fatigue resistance [29,30]. With respect to mineral oils, the plant oils have a lower coefficient of friction and better pitting resistance, but also poorer thermal and oxidative stability [7,31,32]. Shahabuddin et al. [33] have studied the tribological characteristics of Jatropha oil (JO) contaminated bio-lubricant by using Cygnus wear and Four-ball tribo testing machines. Their results show that the addition of Jatropha oil in the base lubricant acted as a very good lubricant additive which reduced the friction and wear scar diameter. Therefore, in this paper, the tribological performance of Rapeseed oil and of Jatropha Curcas L. seed oil in the lubricating steel contact was investigated. Tests were carried out by using a ball-on-flat reciprocatory tribometer for several frequencies and for several normal loads. AISI E52100 steel and X210Cr12 steel have been chosen as material for testing the lubricating properties of the oils. As reported by [34] AISI E52100 steel is used in tribological application as linear guides and rolling bearings due to its high hardness and wear resistance, whereas, the X210Cr12 steel is used for producing of highly stressed moulds, grinding tools [35] or tools for cold forming. Rapeseed Methyl Esther (RME) oil, Hydrotreated Vegetable Oil of Rapeseed (HVO) and raw Jatropha Curcas L. oil

(JCL) were used as lubricant in the tribological tests. According to the standard ASTM D445 - Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity) important oil characteristics as kinematic viscosity, dynamic viscosity, density, flash point and total acid number have been investigated in order to know their chemical and physical properties. For the tribological test, the results were interpreted on the basis of the evolution of the friction coefficient.

1. Material and methods

2.1 Oils and their grown areas

In this paper Rapeseed Methyl Esther (RME) oil, Hydrotreated Vegetable Oil of Rapeseed (HVO) and raw Jatropha Curcas L. (JCL) oil have been investigated and have been used as lubricant in the tribological tests. This research was carried on in the laboratories of the Department of Mechanical Engineering, Chemical and Industrial Design at the Universidad Politécnica de Madrid and in the Applied Mechanic laboratory of the Department of Industrial Engineering at the University of Salerno, on oils provided by Czech University of Life Sciences of Prague. The raw Rapeseed oil is obtained from the seeds of Rapeseed (Brassica napus) belonging to the family Brassicaceae. Rapeseed cultivation is preferred in hilly environments and the main world producers of rapeseed oil are: Canada, China, USA, France, India, Pakistan and Germany. Jatropha Curcas L. is a perennial and poisonous shrub of the Euphorbiaceae family. Its growing areas are subtropical and tropical regions in Africa, Central and South America and South Asia as well. In this research the seeds of Jatropha Curcas L. plants came from Indonesia and have been pressed by Labor Tech MP Test 5.050 machine by applying the pressure of 5 kN and with a deformation speed of 10 mm•min^{-}

[1]. The Crude JCL oil was dark greenish yellow in color. The fatty acid profile of JCL oil, with double bonds Carbons in the chain, is: Palmitic (C16:0), Stearic (C18:0), Arachidic (C20:0), Oleic (C18:1) and Linoleic (C18:2) [36]. The fatty acid profile of RME oil is: Palmitic (C16:0), Stearic (C18:0), Oleic (C18:1), Linoleic (C18:2), Linolenic (C18:3) and Eicosenoic (C20:1) [37]. Chemically hydrotreated vegetable oil (HVO) is mixtures of paraffinic hydrocarbons and is free of sulfur and aromatics where double bonds and oxygen are converted to hydrocarbons by saturation of the double bonds and removal of oxygen (decarboxylation, decarbonylation, dehydration) [19]. As mentioned in [38] at a low hydrotreated reaction temperature, the organic liquid product contained also free fatty acids and triglycerides (i.e. at 260°C, Palmitic acid (C16:0) 0.1wt.%, Stearic acid (C18:0) 0.6wt.%; i.e. at 340°C, Palmitic acid (C16:0) and Stearic acid (C18:0) < 0.05 wt.%)

2.2 Physicochemical Properties of the oils

According to the standard ASTM D445 the kinematic viscosity, dynamic viscosity, density, flash point and total acid number were investigated. In order to know the density of the three oils, a pycnometer of 10 ml was used in a controlled temperature room (15ºC). For the viscosity, the temperature was of 40ºC under ASTM D445-65 recommendation and Afora Cannon-Fenske viscometer (Series 300) was employed [6]. An important property for a fluid, so that is used as a lubricant fluid in industrial applications and also as additive for diesel fuel, is the kinematic viscosity. In fact, this parameter affects the lubrication mechanism and, thus, the wear rate of sliding surfaces. Flash Point Tester, according to Pensky-Martens ASTN D93 IP 34 Semi-Automatic DIN 51758 was employed to determinate the Flash point of the three oils. The flash point is defined as the minimum temperature, at 1 atmosphere pressure, to which a combustible substance in contact with air emits enough vapours so that the inflammation can be produced by providing an energy external trigger. The sample is heated slowly (5ºC/min) and at constant speed with continuous stirring. At regular intervals a small flame in the glass has been introduced by stopping, simultaneously, the agitation. The results, according to the standard ASTM D445, was corrected, using the formula (1), was corrected at a pressure of 760 mmHg because the test was performed at an atmospheric pressure of 703 mmHg.

$$T = T_{obs}(^{o}C) + 0.333 \times [760 - P_{obs}] \qquad (1)$$

The quantity of total acids (TAN) in the oil samples were examined in accordance with ASTM D664. Titrations were carried out using a potentiometric titrator equipped with an integrated stirrer and with standard pH indicator and reference electrodes. As solvent was chosen a mixture of: 2.5 ml of water, 247.5 ml of isopropyl alcohol and 250 ml of chloroform. The titrant was [KOH]= 0.1 mol/L in isopropyl alcohol and the size sample was of 2 mg for FAME and 2 mg for HVO. Each sample was titrated three times.

As for the sample of raw Jatropha Curcas L. oil, in the titration test for the evaluation of the TAN, it is seen that the solution behaved as a buffer solution. This behaviour is due to the proteins presence in the raw oil [39]. An amphiprotic molecule (or ion), like water, amino acids, proteins, can either donate or accept a proton, thus acting either as an acid or a base. This behaviour is called amphiprotic species. $R\text{-}CH(NH_2)\text{-}COOH$ amino acids can donate the acidic proton and/or accept a proton by amine group.

$$R\text{-}CH(NH_2)\text{-}COO^- + H^+ \rightleftharpoons R\text{-}CH(NH_2)\text{-}COOH$$

$$R\text{-}CH(NH_2)\text{-}COOH + H^+ \rightleftharpoons R\text{-}CH(N^+H_3)\text{-}COOH$$

Also, since they can act like an acid or a base, they are amphoteric [40]. For this reason, the raw sample of Jatropha oil was subjected to a protein extraction process before titration. This method, called liquid-liquid extraction [41], is useful to separate the components in a mixture. The method takes advantage of the solubility difference of the components of a mixture between two immiscible or partially miscible liquids and consists in transferring one or more solute(s) contained in a feed solution to another liquid (solvent). As solvents were chosen a mixture of 100ml of chloroform and 4g of raw Jatropha Curcas L seed oil and 40 ml of water in a Separating funnel. The separation process (**Figure 3**) was repeated three times.

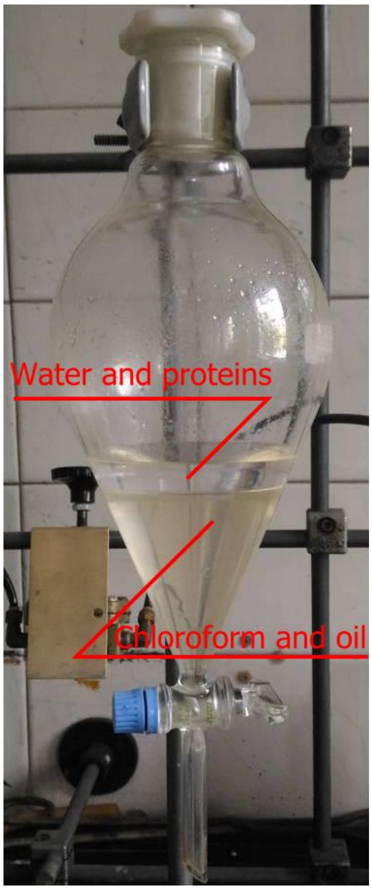

Figure 3: Separating funnel used in liquid-liquid extraction

Once obtained, the separation of the proteins, the chloroform-oil mixture was used as the basis for the solvent in the titration process for calculating the TAN. The results of physicochemical properties are reported in **Table *1*** in results section.

In order to evaluate the behaviour of the dynamic viscosity a verified Dial Brookfield (Viscometer RV) rotational type was used. The Dial Brookfield Viscometer (accuracy ±1% and repeatability ±0.2%) is equipped with a guard leg and a spindle series under

Brookfield Society Engineering recommendation. In general, the Newton's law of viscosity is expressed by:

$$\tau = \mu \cdot \dot{\gamma}^{n} \tag{2}$$

Where τ, μ and $\dot{\gamma}$ are the shear stress, the dynamic viscosity and the velocity gradient respectively. The exponent n can assume values: $0 \leq n < 1$, $n=1$ and $n > 1$ for Pseudoplastic, Newtonian and Dilatant fluid, respectively.

2.3 Tribological tests

In order to obtain an extensive investigation on the oils performance in a wide range of relative velocities we selected an alternative motion tribo-apparatus. Thus, friction tests were carried out using a ball-on-flat Reciprocatory Friction Monitor TR-BIO 282 (Ducom Instruments, Bangalore, India), following a consolidate test procedure [42–46] and repeating each test three times for the reliability. In **Figure 4** the schematic apparatus is represented. An AISI E52100 steel sphere, 10 mm of diameter, was hold in contact against a flat specimen of X210Cr12 steel. In the interface between these two elements the lubricant was deposited. The reciprocating movement of the sphere is guaranteed by a stepper motor and a rocker arm. A load cell at the bottom of the flat specimen records the frictional force.

Different conditions of velocity and load were applied to the apparatus in order to characterize the tribological behaviour of the oils under different situations. The load was selected with values of 10 and 19 N, whereas the oscillation frequency was equal to 10 and 20 Hz. The tests lasted 30 minutes, enough to gain a steady state value of the friction coefficient. With a stroke equal to 8 mm the total distance covered by the ball was equal to 288 and 648 m with 10 Hz and 20 Hz, respectively. The applied pressure was evaluated by using the Hertz's contact theory:

$$r = 0{,}908 \cdot \sqrt[3]{\frac{N}{E^*}\frac{1}{D}} \tag{3}$$

$$\frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} - \frac{1-\nu_2^2}{E_2} \tag{4}$$

$$D = \frac{1}{2}\left(\frac{1}{R_1} + \frac{1}{R_1^{'}} + \frac{1}{R_2} + \frac{1}{R_2^{'}}\right) \tag{5}$$

In (3) *r* is the radius of the contact area and N is the normal load. In (4) E is Young modulus and ν is the Poisson's ratio of the respective materials. In (5) *R* and *R'* are the curvature radius of the materials.

As function of the normal load, applied by the sphere of 10 mm in diameter, the pressure was equal to 660 and 818 MPa. Every test was carried out at room temperature *T*=20 °C, in laboratory air at controlled levels of relative humidity *H*=55±5%. Before each test the specimens were ultrasonically cleaned in clean alcohol and dried thoroughly.

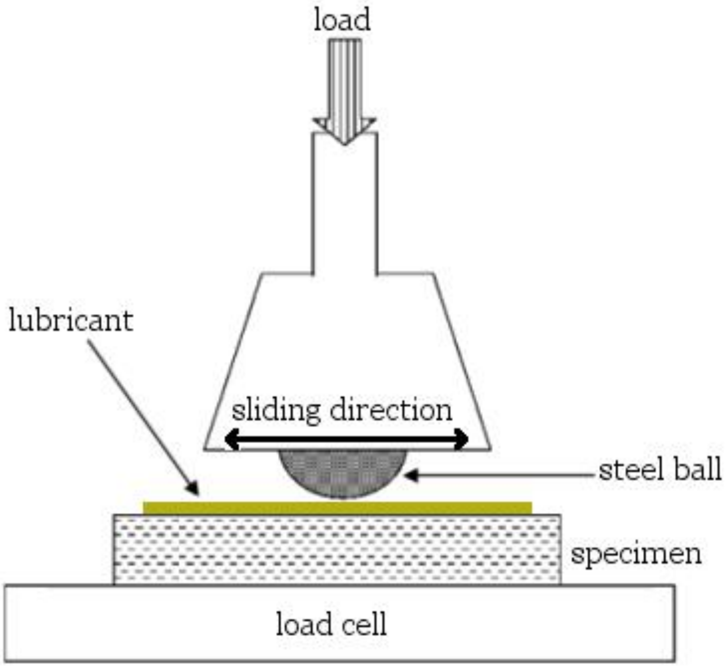

Figure 4 Schematic representation of the reciprocating apparatus.

To estimate wear of the sliding surfaces after the tribo-tests an optical investigation was performed through a topographic surface acquisition carried out with a 3D non-contact optical profilometer, PLu Neox (Sensofar, Terrassa, Spain), which functions either as a confocal microscope [47,48] or as a white light interferometer [49]. The worn surfaces, previously cleaned from debris, washed with ethanol and dried, were scanned using a confocal lens with magnification of 20×. This analysis allowed to evaluate the wear volume and the surface roughness of the worn spheres. To evaluate the wear volume on the spheres the surface was first made plane, which allowed to convert the sphere cap in a wear crater. The chosen roughness parameters were *Ra* and *Rq* that describe the morphology of the worn surface [50,51]

3 Results and Discussions

3.1 Physicochemical properties

The results obtained from the performed physicochemical tests were collected and reported in **Table 1**:

Table 1: Physicochemical properties of three oils.

Properties	**RME**	**HVO**	**Jatropha Curcas L. oil**
Density at 15ºC (kg/m^3)	884.5	780.7	916.9
Kinematic viscosity at 40ºC (cSt)	2.829	4.679	36.605
Flash point at 760 mmHg (ºC)	234±0.5	245±0.5	263±0.5
TAN (mg KOH/g)	0.22	0.08	21.4

The results of the kinematic viscosity and of the TAN show a substantial difference between the two rapeseed based oils (HVO, RME) with the JCL raw oil. In fact, the value of the kinematic viscosity and of the TAN of the JCL raw oil appears to be up to nearly 10 times and 100 times higher than the other two oils (HVO and RME respectively). The results are consistent with those found in scientific literature. In fact,

A. Emil et al. (2010) [52], in their study on the comparative evaluation of physicochemical properties of JCL seed raw oil from different grow areas, found the same results for the kinematic viscosity in terms of order of magnitude. The same results for the kinematic viscosity and for the TAN were found by V. B. Shambhu et al. (2008) [53]. The results indicate that the Transesterification and Hydrogenation reduce the kinematic viscosity to a great extent [53]. The high values of the TAN of the JCL raw oil are caused by the presence of the free fatty acids [54]. From **Table 1**, it can be observed that the value of kinematic viscosity for Jatropha Curcas L. oil presents an order of magnitude higher than the other oils; for the raw Rapeseed oil, the viscosity is reduced by the conversion of the triglyceride oils to esters. In fact, the HVO present a higher viscosity value than RME.

From the same **Table 1**, the results of the flash point of the three oils confirm a high value for the plant oil with respect to the petroleum based oil. Thus considerably reducing the risks of fire in case of a lubricant leak. With respect to the TAN, the **Table 1** shows the lower values of this property for HVO (0.08 mg KOH/g) and for RME (0.22 mg KOH/g). These results are favourable for steel pairs, like those used in the tribo-tests, because a high acid numbers may cause corrosion and poor cold flow properties. In addition, as the TAN for the HVO and RME respect the maximum values assigned by the standard EN 14104 (0.5 mg KOH/g), these oils can be used as additive in the diesel fuels.

The **Figure 5** shows the behaviour of the three oils. For the Jatropha Curcas L. seed oil (red line) the exponent n is 0.962 and it denotes a pseudoplastic behaviour [55]. Whereas, for the RME (blue line) and rapeseed HVO (purple line) it is possible to see two sections of the respective curves: The first one between the shear rate values of 0 s^{-1} to 0.35 s^{-1} and the second one after the value 0.35 s^{-1} till around 1.7 s^{-1}. In both cases, the behaviour is linear, but for the shear rate values higher than 0.35 s^{-1} there is a linear increase of shear stresses [56].

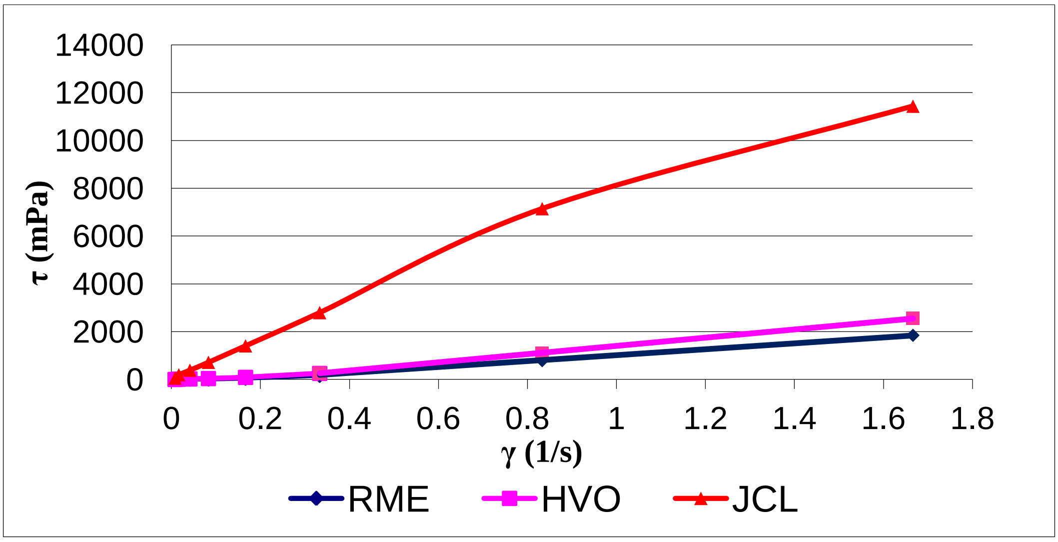

Figure 5: The evolution of the Shear Stress with respect to velocity gradient

3.2 Tribological results

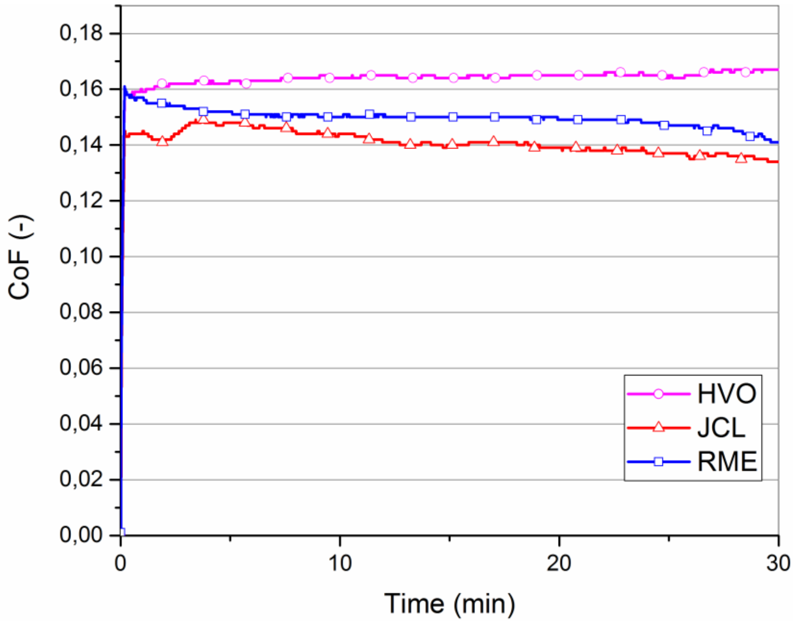

Figure 6: Evolution of the CoF during the tribo-test under lubricated conditions, with a normal load of 10N for 10 Hz.

For exemplificative purpose, in **Figure 6,** it is reported the typical evolution of the coefficient of friction (CoF) for the three oils obtained with 10 N and 10 Hz. This graph shows the evolution of the friction coefficient during the 30 min test, underlining an almost steady state condition reached after the first phase. To estimate a mean friction coefficient and avoid the influence of a transient phase, only the last 20 minutes of the test where considered. The variance of the CoF during this period was also evaluated and it was at least four order of magnitude lower than the mean value, indicating the steadiness of CoF reached. A first glance at this plots already reveals the differences of the three oils under the same conditions, showing that JCL has the lowest CoF.

A statistical analysis leaded to the summary reported in **Figure 7**, the histograms show the CoF mean values – and the relative standard deviation – obtained under the two loads, (a) 10 N and (b)19 N, and compare the results in term of oscillation frequencies (10 Hz and 20 Hz). The bars depict a reduction of the CoF as the frequency – therefore the sliding velocity – rises from 10 Hz to 20 Hz. By comparing the results in term of applied load no trend was found, in other words: higher load does not always mean higher CoF.

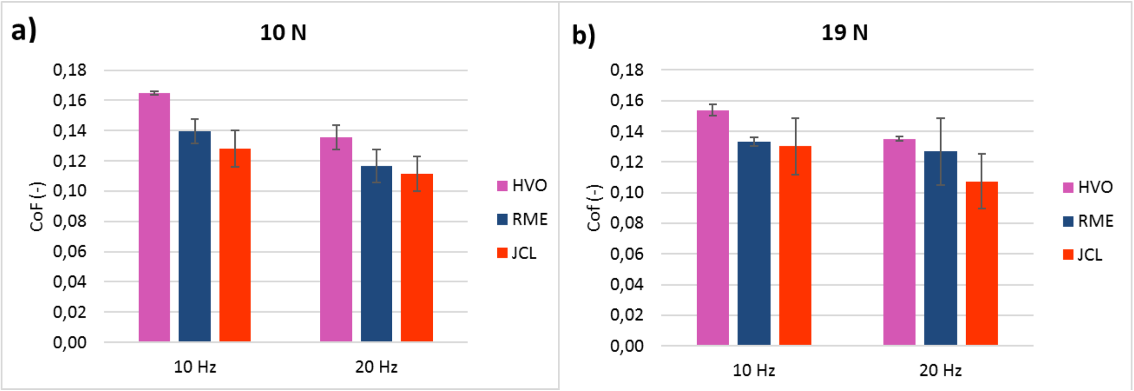

Figure 7: CoF vs Frequency for the three oils under (a) 10 N and (b) 19 N.

Regarding the oils tribo-behaviour it emerges that the lowest values of the CoF are found for the JCL. Thus this oil performs a better lubrication than the other two, reaching a CoF reduction of even 22% in case of 10 N and 10 Hz with respect to the HVO. The latter in fact always presented the highest CoF value. The CoF of RME is placed in between the other two.

The investigated oils contain fatty acids that help the lubricant stick on the sphere when direct contact occurs and helps the lubricant avoid the metal from rubbing while keeping a lubricant film between the two surfaces [57]. Sharma, et al. [58] stated that the fatty acid chains in vegetable oil permitted monolayer film formation with a slippery surface that prevent direct metal-to-metal contact.

The CoF mean value of JCL is 0.13 and 0.11 for 10 Hz and 20 Hz respectively, very little difference is found as the load varied. To the authors best knowledge there are no other researches which studied the friction of this raw oil on an alternative motion apparatus, thus it is hard to compare these results with those obtained by other scientists who used a constant sliding speed. To be thorough, Shahabuddin et al. [33] obtained similar CoF values using a pin-on-disk tribo testing machine for the analysis of a JCL blended at different percentage with SAE 40. CoF values, in their research, varied between 0.10 and 0.22 as function of the blended volume, nevertheless most of the samples gather around 0.15. Shahabuddin stated that the lubricant regime that occurred during the tests was boundary. Shashidhara and Jayaram [59] used a pin-on-disk tribometer to compare the performance of two vegetable oils, namely Pongam and Jatropha. They found CoF values for the raw Jatropha oil varying between 0.05 and 0.07 as function of the normal load applied, which was 70 N, 100 N and 150 N. They also asses a boundary lubrication regime. In the following sections we will demonstrate that our tests (conducted on a reciprocating apparatus) characterize the oils behaviour in all the lubrication regimes (boundary, mixed and elastohydrodynamic).

Regarding the RME, its value oscillates in the range of 0.12 and 0.14, neither in this case a sensible variation nor a trend was found as the load increased. Arnsek and Vizintin [60] tested rapeseed-base oil on SRV high frequency test device that provides ball-on-flat reciprocating motion. In their work they found a strong correlation of pressure-CoF only when moving from 1 GPa to 2 GPa, from the latter to the higher pressure values the CoF varied around 0.12-0.13.

HVO lubricated tests gave the highest CoF values, in every conditions of load and frequency. These values oscillate between 0.14 and 0.17. Hartikka et al. [61] detected a CoF of a hydrotreated vegetable oil greater to 0.175 under a SL-BOCLE test.

In our case 3D topography gained information on the wear of the spheres but no remarkable wear information was found on the harder surface of the X210Cr12 flat specimens. In **Figures 8, 9** and **10**, the worn surfaces and the impression diameters of the AISI E52100 spheres, after tribotests, are reported by using HVO, JCL and RME as lubricants, respectively. Each figure shows the 3D topographies under several conditions: **a)** Load 10N and frequency 10Hz; **b)** Load 10N and frequency 20Hz; **c)** Load 19N and frequency 10Hz; **d)** Load 10N and frequency 10Hz.

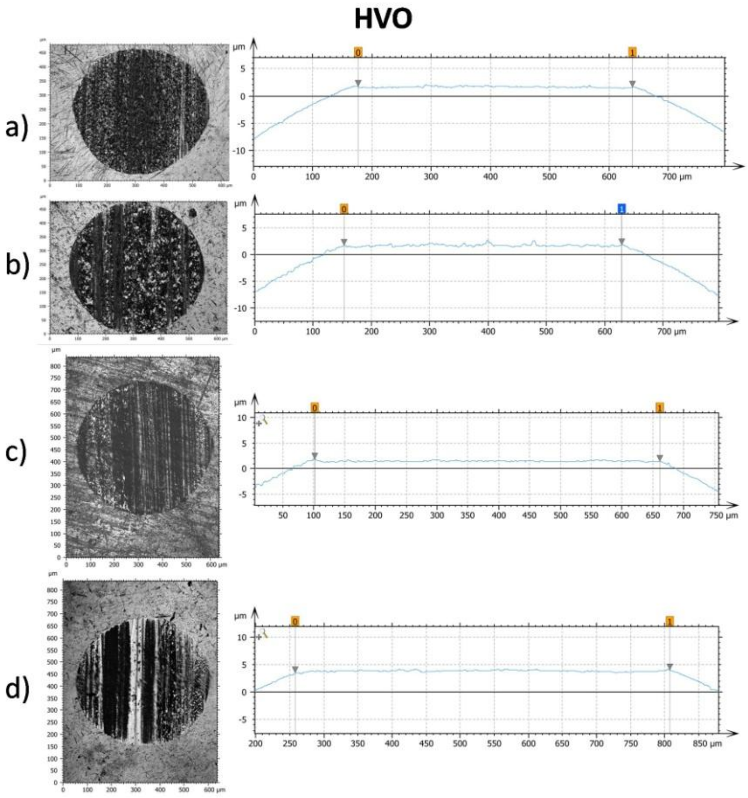

Figure 8: Worm surfaces and impression diameters of the AISI E52100 spheres after tribotests with HVO lubricant: a) Load 10N and frequency 10Hz; b) Load 10N and frequency 20Hz; c)Load 19N and frequency 10Hz; d) Load 10N and frequency 10Hz

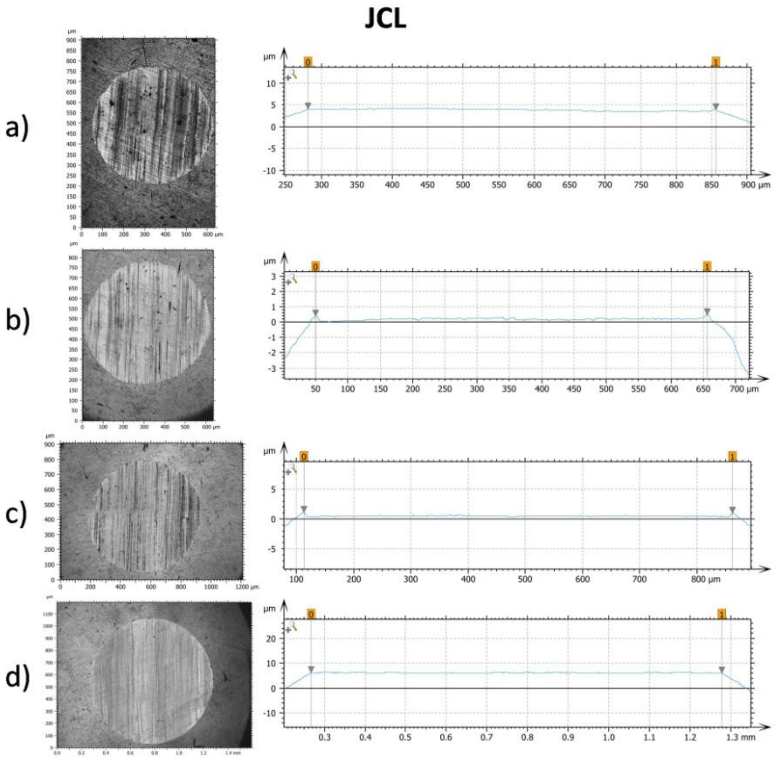

Figure 9: Worm surfaces and impression diameters of the AISI E52100 spheres after tribotests with JCL lubricant: a) Load 10N and frequency 10Hz; b) Load 10N and frequency 20Hz; c)Load 19N and frequency 10Hz; d) Load 10N and frequency 10Hz

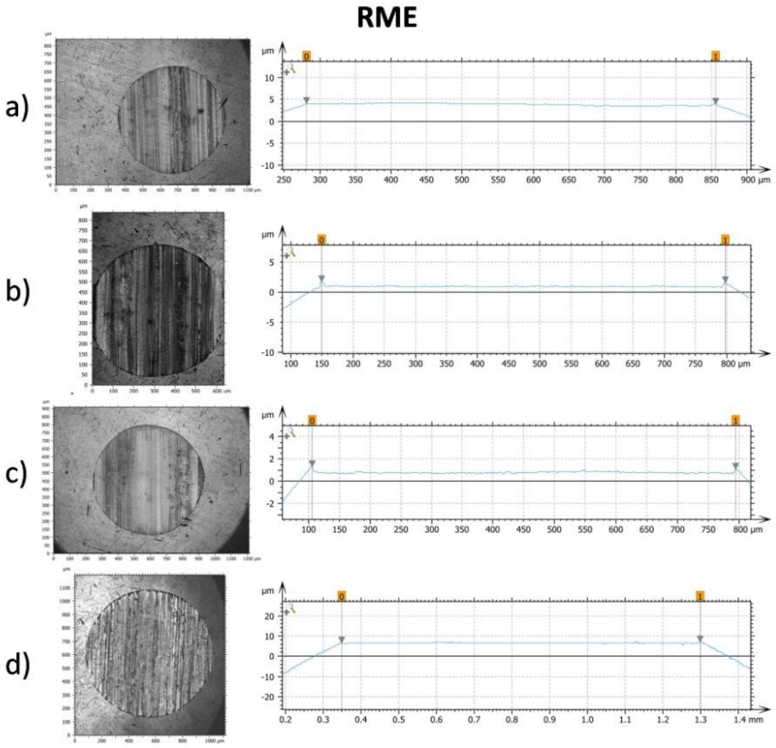

Figure 10: Worm surfaces and impression diameters of the AISI E52100 spheres after tribotests with RME lubricant: a) Load 10N and frequency 10Hz; b) Load 10N and frequency 20Hz; c)Load 19N and frequency 10Hz; d) Load 10N and frequency 10Hz

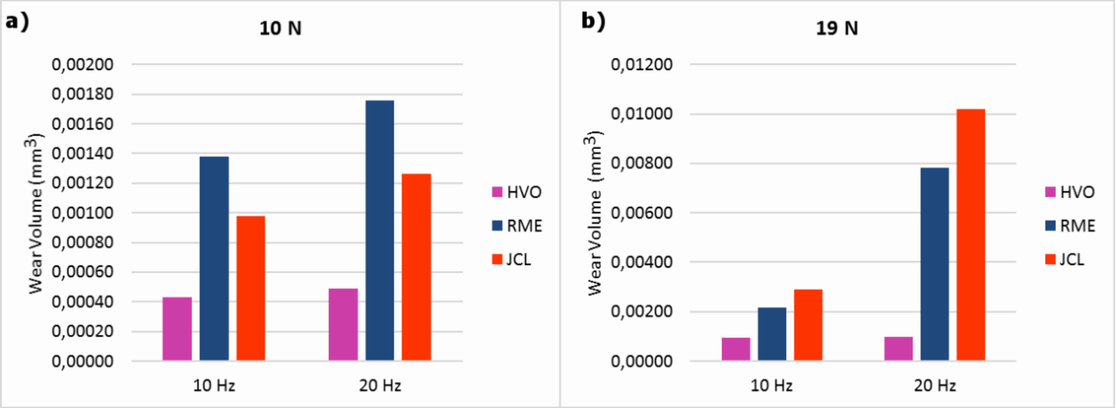

Figure 11: Wear volume for the three oils under (a) 10 N and (b) 19 N.

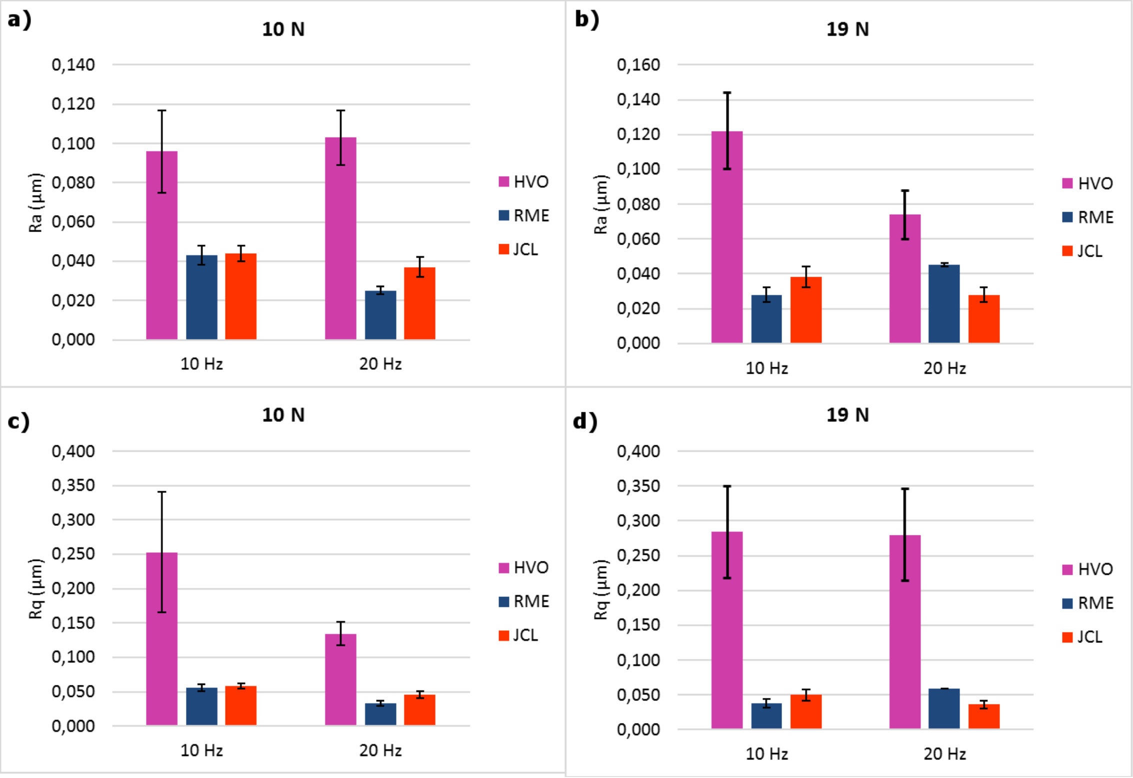

Figure 12: Surface roughness of the worn spheres after tribotests. a) and b) show the Ra values under 10 N and 19 N respectively. c) and d) show the Rq values under 10 N and 19 N.

In **Figure 11** it is shown the wear volume obtained from the topography. As evidenced by the histograms the lowest wear volume recorded among the oils is related to the HVO that, on the contrary, exhibited the highest CoF. Regarding the influence of the oscillation frequency, the wear volume obviously increased as the frequency rises due to the doubling of the total sliding cycles. The increased load as expected also induced a sensible rise of the wear. Another found is that the RME has the worst behaviour under 10 N but not at 19 N, where the JCL took its place. In **Table 2** are reported the wear volume and average impression diameter: d_m. Four different measurements were performed for each impression after the tribotest to evaluate the d_m along four several directions.

Table 2: Wear volume and impression diameter of the worn AISI E52100 spheres after tribotests with three lubricants

		10N			19N		
		d_m (mm)	std	V (mm^3)	d_m (mm)	std	V (mm^3)
HVO	10 Hz	0,460	0,0066	0,00043	0,558	0,0068	0,00091
	20 Hz	0,474	0,0056	0,00049	0,557	0,0063	0,00092
JCL	10 Hz	0,576	0,0053	0,00098	0,739	0,0127	0,00283
	20 Hz	0,607	0,0109	0,00126	1,010	0,0086	0,01054
RME	10 Hz	0,611	0,0026	0,00138	0,685	0,0057	0,00223
	20 Hz	0,651	0,0093	0,00176	0,946	0,0068	0,00782

In **Figure 12** are summarized the roughness values, *Ra* and *Rq*, evaluated on the worn surface of the spheres along a direction orthogonal to the sliding. In these histograms another found is highlighted: whereas the spheres lubricated with HVO had the lower wear they also had the highest surface roughness.

This finding highlights the difference of lubricants showing changes due to the possible reason that the volumetric value of the sphere lubricated with HVO is greater compared to the sphere lubricated with JCL and RME. According to adhesive theory [62], if adhesion occurs at an interface between two solid surfaces, in solid-state contact, the harder asperities adhere mutually and the plastic shearing of these junctions will remove or cut the softer asperities, leaving them stuck on the hard surface. Free fatty acids in vegetable oils permit monolayer film formation on the surface that prevents direct metal-to-metal contact and preserves the surface from damage. The smoother surface of the wear sample in the case of JCL and RME causes a reduction in the COF by maintaining more lubricating oil at the interface of the sliding components with smaller variations in asperity height, thus reducing the metal-to-metal contact [63,64]. The most common wear phenomena were abrasive and adhesive because of the existence of straight grooves along the sliding direction. These grooves occur because the asperities on the hard surface (flat) touched the softer (sphere) and had a close relationship to the thickness of the lubrication film [57].

The high roughness and low wear of the samples lubricated with HVO could find its explanation on a prevalence of adhesive wear, as the lubricant failed to separate the surfaces at low speed – which also lead to the highest CoF –, allowing conjunction of the metals. When a junction is formed between the sliding surfaces, the shearing may occur in several different ways according to the strengths of the two substrates and the junction. If the junction is weaker than the two substrates, shearing will occur at the actual interface where the junction is formed, at which the wear will be very small although the friction may be high [65]. The main reason of the failure to separate the surfaces at low speed is attributable to the low viscosity value. On the other hand, to evaluate the influence of the oil viscosity on the friction it should be known the variation of the viscosity with the pressure, since the maximum pressure in hard EHD contact can reach 3–4 GPa with the minimum film thickness is in the range 0.1–1 mm. The elastic deformations in such a contact are several orders of magnitude larger than the minimum film thickness and the viscosity of the lubricant can rise of 10 orders of magnitude within the meatus [24].

Under different boundary lubrication conditions, the wear process may be influenced by many other factors beyond adhesion, such as chemical reactions, oxidation, corrosion, fatigue, and scuffing [66], all of which requires further investigation. In fact, having a higher friction coefficient (as for the HVO) can lead to greater interface temperature, that will promote the formation of an oxide layer [67]. The oxide layer would offers a certain amount of protection from wear [68].

Figure 13 shows the Stribeck curves for the three oils with the standard deviation, the minimum, the maximum and the mean values of the friction coefficient *vs.* the Stribeck parameter in the case of test realized with normal load of 10 N and frequency of 10 Hz. The graphs were obtained considering the Stribeck parameter, that was evaluated as:

$$\eta \cdot \frac{U}{W} \tag{6}$$

where η is the absolute viscosity, U is the sliding velocity and W is the normal load.

The above mentioned Stribeck curves show how the CoF varies during the acceleration of the ball, namely the first half of the stroke, by considering the cycles after the transient phase. In the same figure it is possible to identify three areas (highlighted by I, II and III), that represents the three different lubrication regimes: I for the Extreme Pressure (EP) lubrication; II for mixed lubrication; III for Elastohydrodynamic (EHD) lubrication [69]. This classification is due to the kind of contact, that is a nonconformal contact. In order to estimate a comparison of CoF global variation – during all lubrication regimes – their mean values were evaluated along the whole cycle of the sphere. In fact, the distribution of the lubrication mechanism along the stroke is the same for the three oils for each considered frequencies.

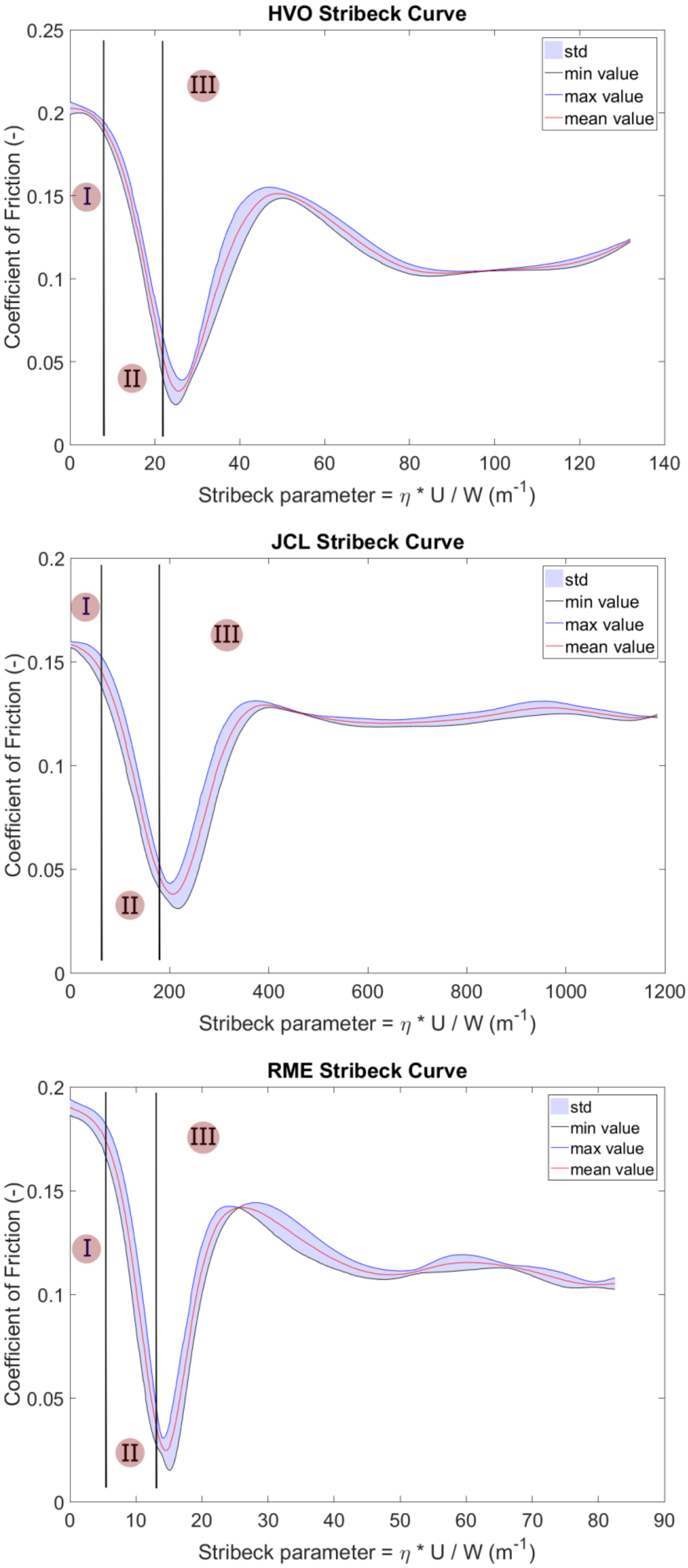

Figure 13: Stribeck curves for HVO, JCL and RME respectively.

2. Conclusions

The tribological performances of raw Jatropha Curcas L. seeds oil, Rapeseed Methyl Ester oil and Hydrotreated Rapeseed oil in the lubricating contact pair AISI E52100 steel sliding against X210Cr12 steel were investigated. The physicochemical properties of the three oils like density, kinematic viscosity, dynamic viscosity, flash point and total acid number were investigated. In fact, the chemical composition combined with the rheological properties affects the performance of these lubricants in the lubrication regimes.

The tribological tests were conducted by using a reciprocating pin on flat tribometer varying the oscillation frequency (10 and 20 Hz). The normal load was set to 10 N and 19 N, the stroke to 8 mm and the test time to 30 min.

The oil exhibited physicochemical properties that allow favourably employment as lubricant feedstock in many industrial applications.

From a tribological point of view the following conclusions can be addressed:

- the use of a reciprocating friction tribometer allowed to investigate the complete tribo-behaviour of the oils passing alternatively through the different lubrication regimes (boundary, mixed and elastohydrodynamic), as evidenced by the Stribeck curves obtained;
- the mean values of the friction coefficient in all tests, stays in the range of 0.11-0.17, which is a relative low range if compared with raw petroleum based oil; this confirms that the fatty acids contained in the oils help the lubricant to stick on the sphere;
- JCL has the lowest CoF among the three oils examined, followed by RME and HVO. It is due to the high amount of stearic acid, which is known to have the most significant influence on friction reduction [70]. In fact, as reporting in [36] the

amount of stearic acid in JCL oil is of 17 wt.%, while for the RME this quantity is of 0.9 wt.%. The fact that low friction does not necessarily mean low wear was emphasised over sixty years ago [71]. This fact appears in the result of the friction coefficient and wear loss volume for the HVO that produced the lowest wear volume with the highest CoF. It can be explained through the presence of low quantity of Palmitic acid and stereatic acid. In fact, the anti-wear behaviour of fatty acids is the result of complex interactions between molecules of the acid and particular types of hydrocarbons [72];

- topography analysis gained deeper insight on the tribo-performance of the oils, discovering a sensible lower wear of the sphere lubricated by HVO, at the same time these sphere presented the highest roughness values. This suggests a prevalence of adhesive wear, as the lubricant failed to separate the surfaces at low speed;

Acknowledgements

The authors gratefully acknowledge Francisco Fernández and Antonio Nieto-Márquez Ballesteros for their help to perform the oil chemical analysis and to check the results in the laboratory of chemistry at ETSIDI-UPM.

References

[1] J.O. Metzger, A. Hüttermann, Sustainable global energy supply based on lignocellulosic biomass from afforestation of degraded areas, Naturwissenschaften. 96 (2009) 279–288. doi:10.1007/s00114-008-0479-4.

[2] J.C.O. Santos, I.M.G. Santos, M.M. Conceição, S.L. Porto, M.F.S. Trindade, A.G. Souza, S. Prasad, V.J. Fernandes Jr., A.S. Araújo, Thermoanalytical, kinetic and rheological parameters of commercial edible vegetable oils, J. Therm. Anal. Calorim. 75 (2004) 419–428. doi:10.1023/B:JTAN.0000027128.62480.db.

[3] P. Nagendramma, S. Kaul, Development of ecofriendly/biodegradable lubricants: An overview, Renew. Sustain. Energy Rev. 16 (2012) 764–774. doi:10.1016/j.rser.2011.09.002.

[4] C. Puscas, G. Bandur, D. Modra, R. Nutiu, Consideration about using plant oils in lubricants, in: World Tribol. Congr. III, Washington, D.C., USA, 2005: pp. 915–916.

[5] N.S. Battersby, The biodegradability and microbial toxicity testing of lubricants – some recommendations, Chemosphere. 41 (2000) 1011–1027. doi:10.1016/S0045-6535(99)00517-2.

[6] A. Ruggiero, R. D'Amato, M. Merola, P. Valášek, M. Müller, On the Tribological Performance of Vegetal Lubricants: Experimental Investigation on Jatropha Curcas L. oil, Procedia Eng. 149 (2016) 431–437. doi:10.1016/j.proeng.2016.06.689.

[7] B. Kržan, J. Vižintin, Tribological properties of an environmentally adopted universal tractor transmission oil based on vegetable oil, Tribol. Int. 36 (2003) 827–833. doi:10.1016/S0301-679X(03)00100-2.

[8] A.K. Agarwal, Biofuels (alcohols and biodiesel) applications as fuels for internal

combustion engines, Prog. Energy Combust. Sci. 33 (2007) 233–271. doi:10.1016/j.pecs.2006.08.003.

[9] A. Kumar, S. Sharma, An evaluation of multipurpose oil seed crop for industrial uses (Jatropha curcas L.): A review, Ind. Crops Prod. 28 (2008) 1–10. doi:10.1016/j.indcrop.2008.01.001.

[10] K. Sunde, A. Brekke, B. Solberg, Environmental Impacts and Costs of Hydrotreated Vegetable Oils, Transesterified Lipids and Woody BTL—A Review, Energies. 4 (2011) 845–877. doi:10.3390/en4060845.

[11] D.Y.C. Leung, X. Wu, M.K.H. Leung, A review on biodiesel production using catalyzed transesterification, Appl. Energy. 87 (2010) 1083–1095. doi:10.1016/j.apenergy.2009.10.006.

[12] A. Adhvaryu, S.. Erhan, J.. Perez, Tribological studies of thermally and chemically modified vegetable oils for use as environmentally friendly lubricants, Wear. 257 (2004) 359–367. doi:10.1016/j.wear.2004.01.005.

[13] M.A.R. Meier, J.O. Metzger, U.S. Schubert, Plant oil renewable resources as green alternatives in polymer science, Chem. Soc. Rev. 36 (2007) 1788. doi:10.1039/b703294c.

[14] R. Becker, A. Knorr, An evaluation of antioxidants for vegetable oils at elevated temperatures, Lubr. Sci. 8 (1996) 95–117. doi:10.1002/ls.3010080202.

[15] A. Adhvaryu, S.. Erhan, Epoxidized soybean oil as a potential source of high-temperature lubricants, Ind. Crops Prod. 15 (2002) 247–254. doi:10.1016/S0926-6690(01)00120-0.

[16] B.K. Sharma, A. Adhvaryu, Z. Liu, S.Z. Erhan, Chemical modification of vegetable oils for lubricant applications, J. Am. Oil Chem. Soc. 83 (2006) 129–136. doi:10.1007/s11746-006-1185-z.

[17] N.N.A.N. Yusuf, S.K. Kamarudin, Z. Yaakub, Overview on the current trends in biodiesel production, Energy Convers. Manag. 52 (2011) 2741–2751. doi:10.1016/j.enconman.2010.12.004.

[18] J. Zhang, L. Jiang, Acid-catalyzed esterification of Zanthoxylum bungeanum seed oil with high free fatty acids for biodiesel production, 2008. doi:10.1016/j.biortech.2008.05.004.

[19] T.N. Kalnes, T. Marker, D.R. Shonnard, K.P. Koers, Green diesel production by hydrorefining renewable feedstocks, Biofuels Technol. (2008) 7–11.

[20] R. Arvidsson, S. Persson, M. Fröling, M. Svanström, Life cycle assessment of hydrotreated vegetable oil from rape, oil palm and Jatropha, J. Clean. Prod. 19 (2011) 129–137. doi:10.1016/j.jclepro.2010.02.008.

[21] B. Donnis, R.G. Egeberg, P. Blom, K.G. Knudsen, Hydroprocessing of Bio-Oils and Oxygenates to Hydrocarbons. Understanding the Reaction Routes, Top. Catal. 52 (2009) 229–240. doi:10.1007/s11244-008-9159-z.

[22] I.I. Ştefãnescu, I.I. Ştefãnescu, C. Calomir, G. Chiritã, On the future of biodegradable vegetable lubricants used for industrial trybosistems., Ann. Dunarea Jos Univ. Galati, Fascicle VIII Tribol. 7 (2002) 94–98.

[23] H.M. Mobarak, E. Niza Mohamad, H.H. Masjuki, M.A. Kalam, K.A.H. Al Mahmud, M. Habibullah, A.M. Ashraful, The prospects of biolubricants as alternatives in automotive applications, Renew. Sustain. Energy Rev. 33 (2014) 34–43. doi:10.1016/j.rser.2014.01.062.

[24] E. Höglund, Influence of lubricant properties on elastohydrodynamic lubrication, Wear. 232 (1999) 176–184. doi:10.1016/S0043-1648(99)00143-X.

[25] M.W. Sulek, A. Kulczycki, A. Malysa, Assessment of lubricity of compositions of fuel oil with biocomponents derived from rape-seed, Wear. 268 (2010) 104–

108. doi:10.1016/j.wear.2009.07.004.

[26] A.S.M.A. Haseeb, S.Y. Sia, M.A. Fazal, H.H. Masjuki, Effect of temperature on tribological properties of palm biodiesel, Energy. 35 (2010) 1460–1464. doi:10.1016/j.energy.2009.12.001.

[27] S. Asadauskas, J.H. Perez, J.L. Duda, Lubrication properties of castor oil - Potential basestock for biodegradable lubricants, Lubr. Eng. 53 (1997) 35–40.

[28] S. Asadauskas, J.. Perez, J.L. Duda, Oxidative stability and antiwear properties of high oleic vegetable oils, Lubr. Eng. 52 (1996) 877–882.

[29] M. Kozma, Investigation into the scuffing load capacity of environmentally-friendly lubricating oils, J. Synth. Lubr. 14 (1997) 249–258. doi:10.1002/jsl.3000140304.

[30] S. Odi-Owei, Tribological properties of some vegetable oils and fats Lubr, Lubr. Eng. 45 (n.d.) 685–690.

[31] A. Arnšek, J. Vižintin, Lubricating properties of rapeseed-based oils, J. Synth. Lubr. 16 (2000) 281–296. doi:10.1002/jsl.3000160402.

[32] A. Arnsek, J. Vižintin, Scuffing load capacity of rapeseed-based oils, Lubr. Eng. 36 (2003) 827–833.

[33] M. Shahabuddin, H.H. Masjuki, M.A. Kalam, M.M.K. Bhuiya, H. Mehat, Comparative tribological investigation of bio-lubricant formulated from a non-edible oil source (Jatropha oil), Ind. Crops Prod. 47 (2013) 323–330. doi:10.1016/j.indcrop.2013.03.026.

[34] M. Koga, E.C. Santos, T. Honda, K. Kida, T. Shibukawa, Investigation of wear in induction-heated AISI E 52100 steel bars under reciprocating motion, Int. J. Mater. Prod. Technol. 44 (2012) 240. doi:10.1504/IJMPT.2012.050185.

[35] T. Bakša, T. Kroupa, P. Hanzl, M. Zetek, Durability of Cutting Tools during

Machining of Very Hard and Solid Materials, Procedia Eng. 100 (2015) 1414–1423. doi:10.1016/j.proeng.2015.01.511.

[36] A. Kumar Tiwari, A. Kumar, H. Raheman, Biodiesel production from jatropha oil (Jatropha curcas) with high free fatty acids: An optimized process, Biomass and Bioenergy. 31 (2007) 569–575. doi:10.1016/j.biombioe.2007.03.003.

[37] J.W. Goodrum, D.P. Geller, Influence of fatty acid methyl esters from hydroxylated vegetable oils on diesel fuel lubricity, Bioresour. Technol. 96 (2005) 851–855. doi:10.1016/j.biortech.2004.07.006.

[38] P. Šimáček, D. Kubička, G. Šebor, M. Pospíšil, Hydroprocessed rapeseed oil as a source of hydrocarbon-based biodiesel, Fuel. 88 (2009) 456–460. doi:10.1016/j.fuel.2008.10.022.

[39] E.T. Akintayo, Characteristics and composition of Parkia biglobbossa and Jatropha curcas oils and cakes, Bioresour. Technol. 92 (2004) 307–310. doi:10.1016/S0960-8524(03)00197-4.

[40] R.H. Petrucci, W.S. Harwood, F.G. Herring, General chemistry : principles and modern applications., Prentice Hall, 2002.

[41] C. Tzia, G. Liadakis, Extraction optimization in food engineering, Marcel Dekker, Inc, 2003.

[42] A. Ruggiero, R. D’Amato, E. Gómez, Experimental analysis of tribological behavior of UHMWPE against AISI420C and against TiAl6V4 alloy under dry and lubricated conditions, Tribol. Int. 92 (2015) 154–161. doi:10.1016/j.triboint.2015.06.005.

[43] A. Ruggiero, R. D’Amato, E. Gómez, M. Merola, Experimental comparison on tribological pairs UHMWPE/TIAL6V4 alloy, UHMWPE/AISI316L austenitic stainless and UHMWPE/AL2O3 ceramic, under dry and lubricated conditions,

Tribol. Int. 96 (2016) 349–360. doi:10.1016/j.triboint.2015.12.041.

[44] A. Ruggiero, P. Valasek, M. Merola, Friction and wear behaviors of Al/Epoxy composites during reciprocating sliding test, Manuf. Technol. 15 (2015) 684–689.

[45] A. Ruggiero, M. Merola, P. Carlone, V.-M. Archodoulaki, Tribo-mechanical characterization of reinforced epoxy resin under dry and lubricated contact conditions, Compos. Part B Eng. 79 (2015) 595–603. doi:10.1016/j.compositesb.2015.05.015.

[46] A. Ruggiero, M. Mindas, L. Knapcíková, Tribodiagnostic investigation on oil filtration: results from a novel apparatus, Ind. Lubr. Tribol. 68 (2016) 689–695. doi:10.1108/ILT-03-2016-0053.

[47] W. Kapłonek, K. Nadolny, G.M. Królczyk, The Use of Focus-Variation Microscopy for the Assessment of Active Surfaces of a New Generation of Coated Abrasive Tools, Meas. Sci. Rev. 16 (2016) 42–53. doi:10.1515/msr-2016-0007.

[48] M. Merola, A. Ruggiero, J.S. De Mattia, S. Affatato, On the tribological behavior of retrieved hip femoral heads affected by metallic debris. A comparative investigation by stylus and optical profilometer for a new roughness measurement protocol, Measurement. 90 (2016) 365–371. doi:10.1016/j.measurement.2016.05.003.

[49] L. Blunt, X.Q. Jiang, Three dimensional measurement of the surface topography of ceramic and metallic orthopaedic joint prostheses., J. Mater. Sci. Mater. Med. 11 (2000) 235–46. http://www.ncbi.nlm.nih.gov/pubmed/15348038 (accessed February 20, 2016).

[50] S.A. Jaber, A. Ruggiero, S. Battaglia, S. Affatato, On the roughness measurement

on knee prostheses., Int. J. Artif. Organs. 38 (2015) 39–44. doi:10.5301/ijao.5000371.

[51] P. Hreha, A. Radvanska, L. Knapcikova, G.M. Królczyk, S. Legutko, J.B. Królczyk, S. Hloch, P. Monka, Roughness Parameters Calculation By Means Of On-Line Vibration Monitoring Emerging From AWJ Interaction With Material, Metrol. Meas. Syst. 22 (2015) 315–326. doi:10.1515/mms-2015-0024.

[52] A. Emil, Z. Yaakob, M.N. Satheesh Kumar, J.M. Jahim, J. Salimon, Comparative Evaluation of Physicochemical Properties of Jatropha Seed Oil from Malaysia, Indonesia and Thailand, J. Am. Oil Chem. Soc. 87 (2010) 689–695. doi:10.1007/s11746-009-1537-6.

[53] V.B. Shambhu, T. Bhattacharya, L. Nayak, S. Das, Studies on Characterization of Raw Jatropha Oil and its Biodiesels with Relevance of Diesel, Int. J. Emerg. Technol. Adv. Eng. 3 (2002) 48–54.

[54] H. Wang, H. Tang, J. Wilson, S.O. Salley, K.Y.S. Ng, Total Acid Number Determination of Biodiesel and Biodiesel Blends, J. Am. Oil Chem. Soc. 85 (2008) 1083–1086. doi:10.1007/s11746-008-1289-8.

[55] C. Georgescu, L.C. Solea, L. Deleanu, Rheological Aspects Of Corn Oil And Rapeseed Oil, J. Balk. Tribol. Assoc. 21 (2016) 912–921.

[56] R.A. Candeia, M.C.D. Silva, J.R. Carvalho Filho, M.G.A. Brasilino, T.C. Bicudo, I.M.G. Santos, A.G. Souza, Influence of soybean biodiesel content on basic properties of biodiesel–diesel blends, Fuel. 88 (2009) 738–743. doi:10.1016/j.fuel.2008.10.015.

[57] N. Noorawzi, S. Samion, Tribological Effects of Vegetable Oil as Alternative Lubricant: A Pin-on-Disk Tribometer and Wear Study, Tribol. Trans. 59 (2016) 831–837. doi:10.1080/10402004.2015.1108477.

[58] B.K. Sharma, K.M. Doll, S.Z. Erhan, Ester hydroxy derivatives of methyl oleate: Tribological, oxidation and low temperature properties, Bioresour. Technol. 99 (2008) 7333–7340. doi:10.1016/j.biortech.2007.12.057.

[59] Y.M. Shashidhara, S.R. Jayaram, Tribological studies on AISI 1040 with raw and modified versions of pongam and jatropha vegetable oils as lubricants, Adv. Tribol. 2012 (2012). doi:10.1155/2012/560175.

[60] A. Arnsek, J. Vizintin, Pitting resistance of rapeseed-based oils, Lubr. Eng. 57 (2001) 17–22.

[61] T. Hartikka, M. Kuronen, U. Kiiski, Technical Performance of HVO (Hydrotreated Vegetable Oil) in Diesel Engines, in: 2012. doi:10.4271/2012-01-1585.

[62] D.H. Buckley, Surface effects in adhesion, friction, wear, and lubrication, Elsevier Science, 1981. https://books.google.it/books?id=62WYwqySS2QC.

[63] M. Kalin, S. Jahanmir, L.K. Ives, Effect of counterface roughness on abrasive wear of hydroxyapatite, Wear. 252 (2002) 679–685. doi:10.1016/S0043-1648(02)00028-5.

[64] U. Dulias, L. Fang, K.-H. Zum Gahr, Effect of surface roughness of self-mated alumina on friction and wear in isooctane-lubricated reciprocating sliding contact, Wear. 252 (2002) 351–358. doi:10.1016/S0043-1648(01)00900-0.

[65] J. Zhang, Y. Meng, Boundary lubrication by adsorption film, Friction. 3 (2015) 115–147. doi:10.1007/s40544-015-0084-4.

[66] A. Beerbower, Boundary lubrication-scientific and technical forecast report, 1972.

[67] A.F. Nurul, S. Syahrullail, Improvement of Lubrication Performance of RBD Palm Stearin as Alternative Lubricant under Different Sliding Speeds, Strojniški

Vestn. - J. Mech. Eng. (2015) 1–11.

[68] I. Gunes, T. Uygunoglu, M. Erdogan, Effect of Sintering Duration on Some Properties of Pure Magnesium, Powder Metall. Met. Ceram. 54 (2015) 156–165. doi:10.1007/s11106-015-9693-8.

[69] J. Frene, T. Cicone, Friction in Lubricated Contacts, in: J. LeMaitre (Ed.), Handb. Mater. Behav. Model., Academic Press, 2001: p. 1200.

[70] M.T. Siniawski, N. Saniei, B. Adhikari, L. Doezema, Influence of Fatty Acid Composition on the Tribiological Performance of Two Vegetable-Based Lubricants, J. Synth. Lubr. 25 (2008) 45–55. doi:10.1002/jsl.

[71] R.G. Larsen, G.L. Perry, Investigation of friction and wear under quasihydrodynamic conditions, Trans. ASME. 67 (1945) 45–49.

[72] C. Kajdas, M. Majzner, Boundary lubrication of low-sulphur diesel fuel in the presence of fatty acids, Lubr. Sci. 14 (2001) 83–108. doi:10.1002/ls.3010140107.

FIGURES

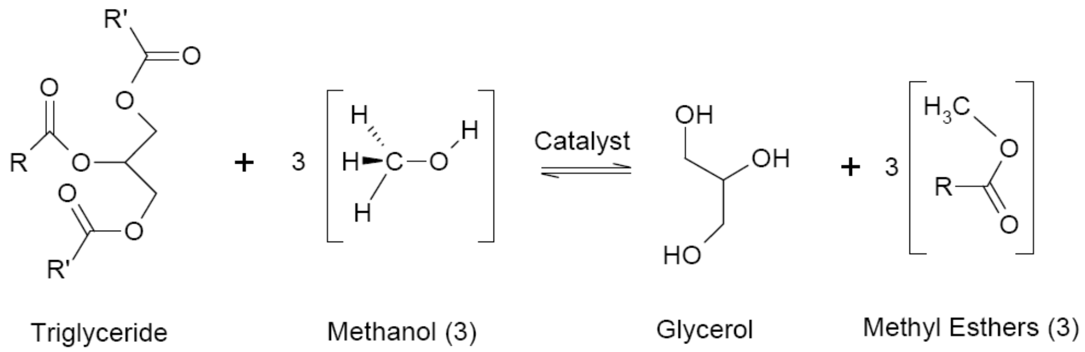

Figure 1: Transesterification reaction

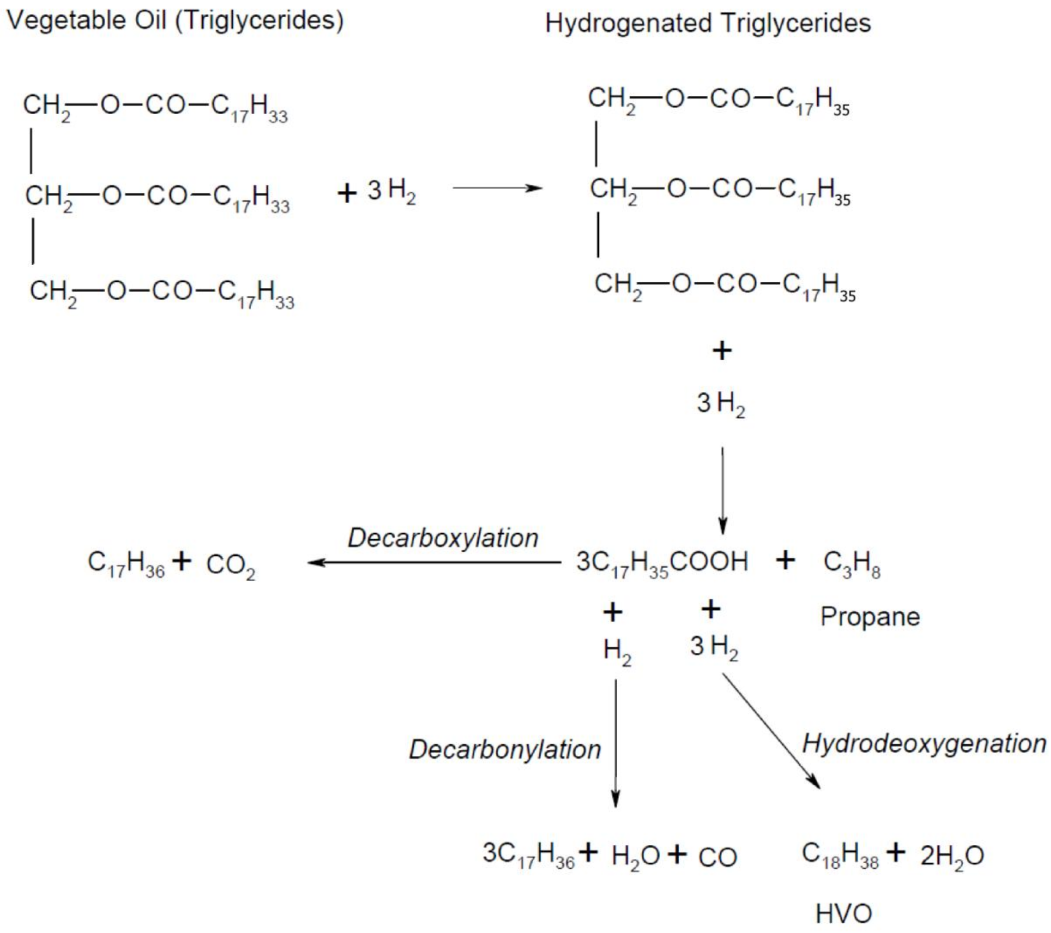

Figure 2: An example of Hydrotreated to obtain HVO

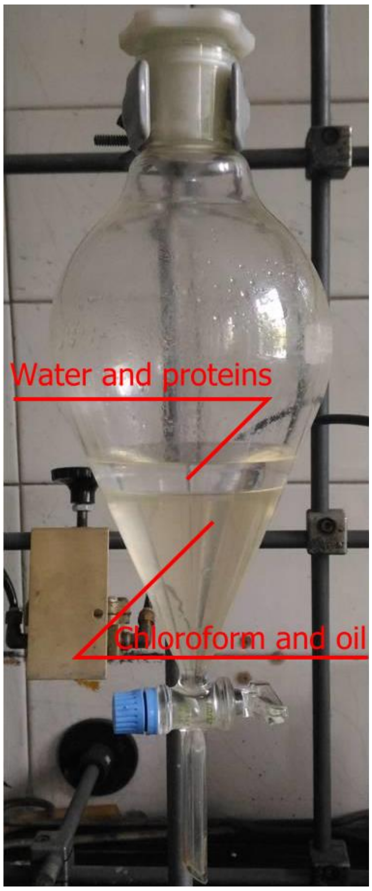

Figure 3: Separating funnel used in liquid-liquid extraction

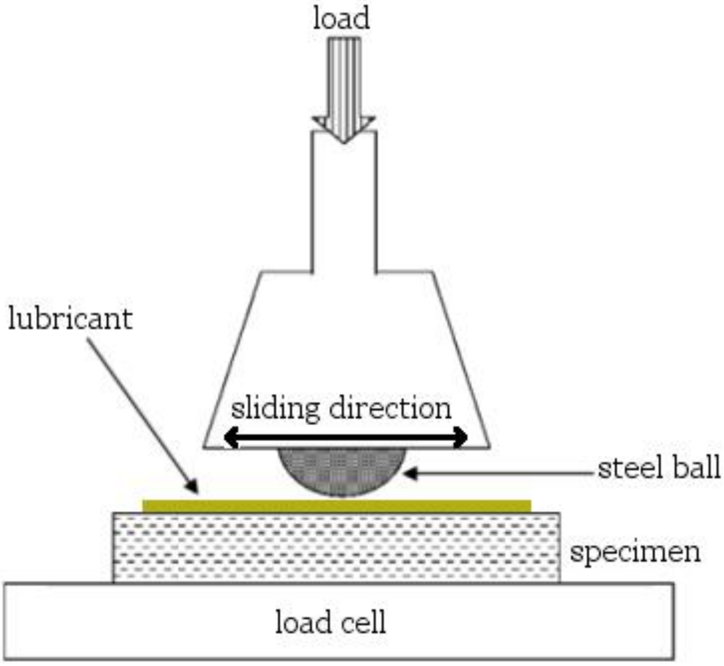

Figure 4 Schematic representation of the reciprocating apparatus.

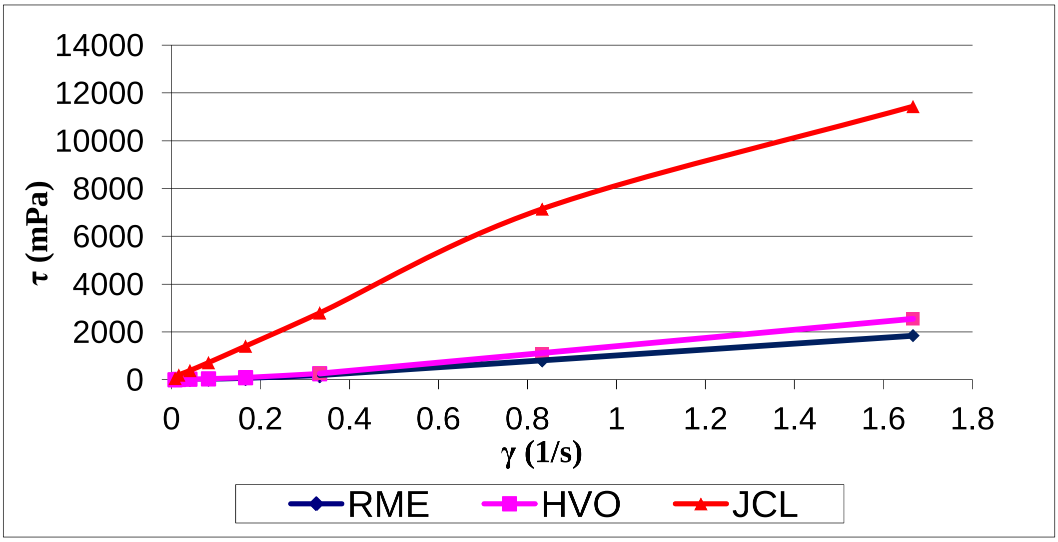

Figure 5: The evolution of the Shear Stress with respect to velocity gradient

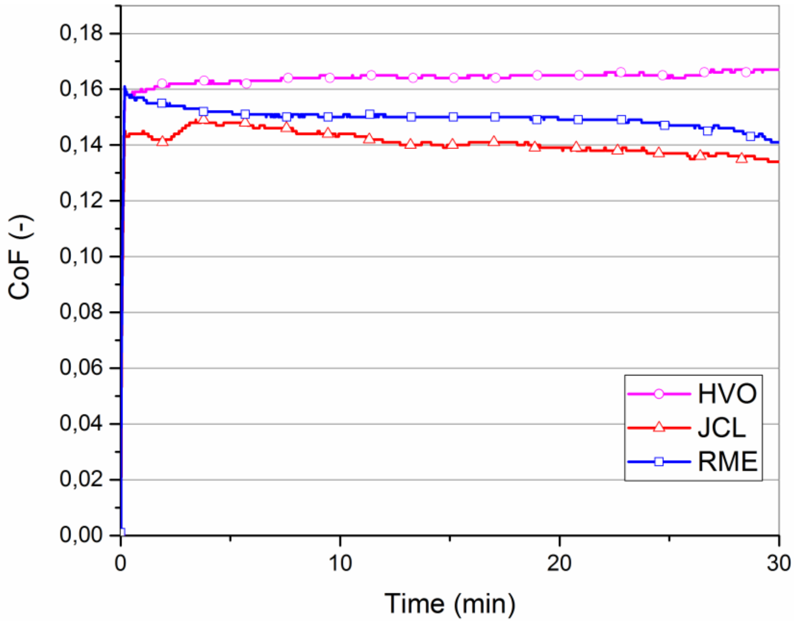

Figure 6: Evolution of the CoF during the tribo-test under lubricated conditions, with a normal load of 10N for 10 Hz.

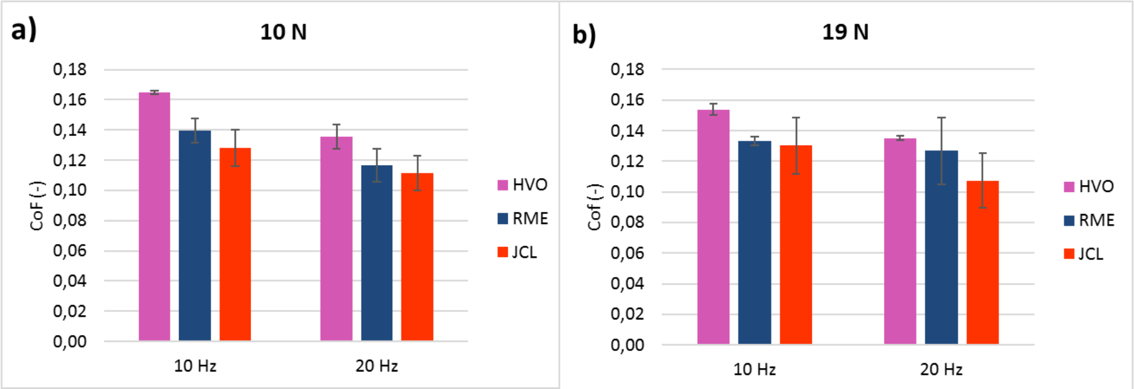

Figure 7: CoF vs Frequency for the three oils under (a) 10 N and (b) 19 N.

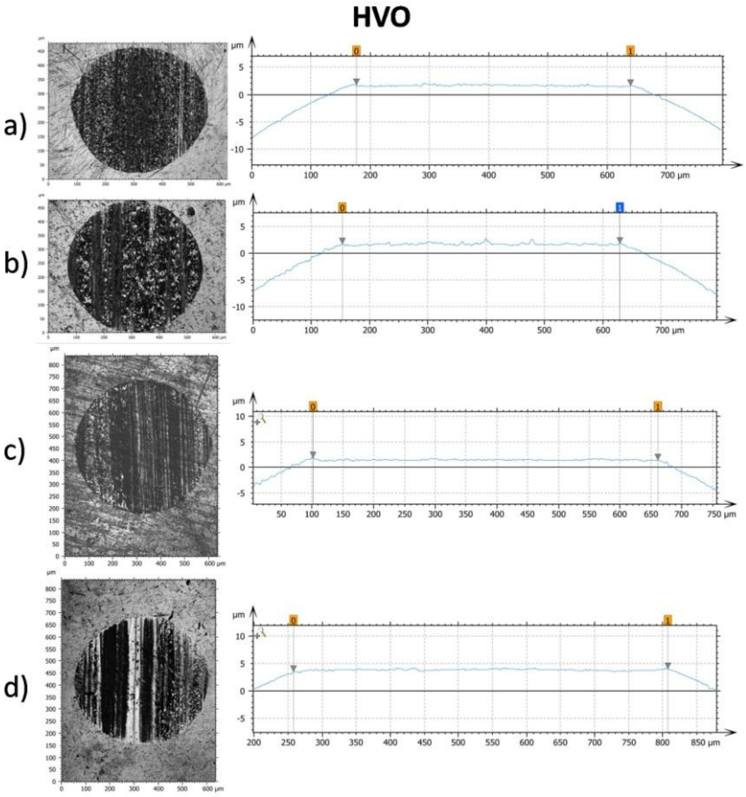

Figure 8: Worm surfaces and impression diameters of the AISI E52100 spheres after tribotests with HVO lubricant: a) Load 10N and frequency 10Hz; b) Load 10N and frequency 20Hz; c)Load 19N and frequency 10Hz; d) Load 10N and frequency 10Hz

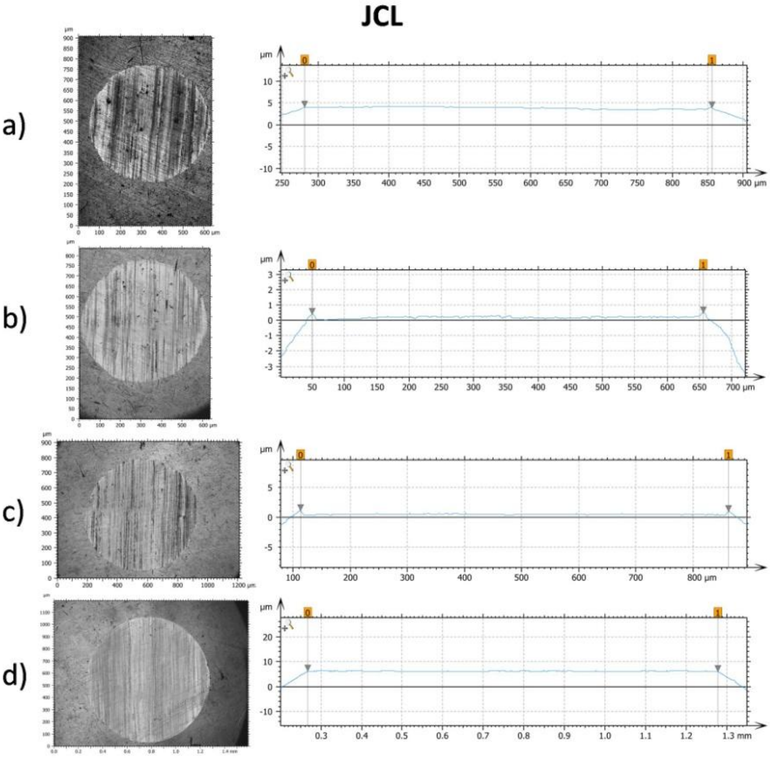

Figure 9: Worm surfaces and impression diameters of the AISI E52100 spheres after tribotests with JCL lubricant: a) Load 10N and frequency 10Hz; b) Load 10N and frequency 20Hz; c)Load 19N and frequency 10Hz; d) Load 10N and frequency 10Hz

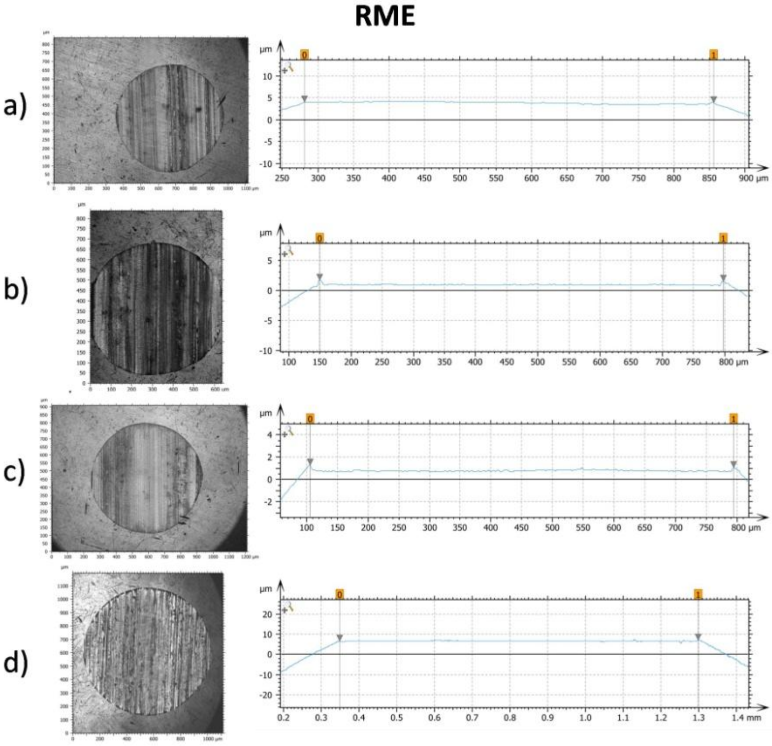

Figure 10: Worm surfaces and impression diameters of the AISI E52100 spheres after tribotests with RME lubricant: a) Load 10N and frequency 10Hz; b) Load 10N and frequency 20Hz; c)Load 19N and frequency 10Hz; d) Load 10N and frequency 10Hz

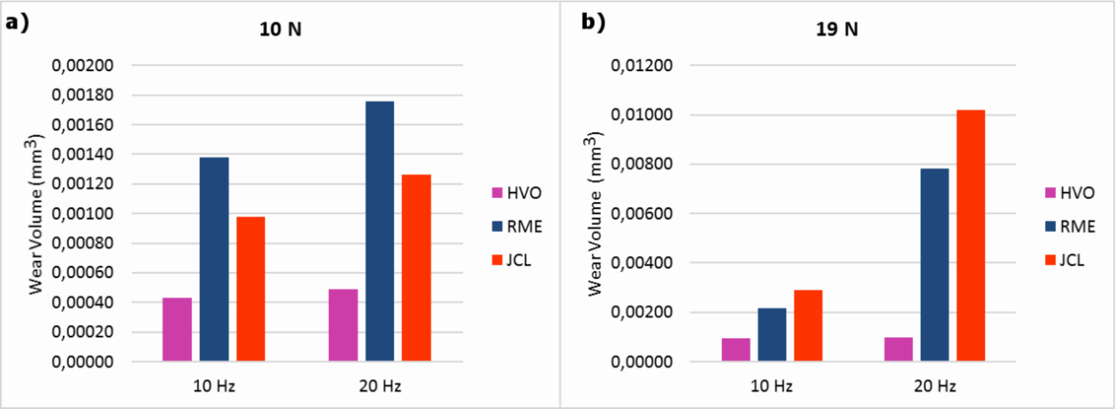

Figure 11: Wear volume for the three oils under (a) 10 N and (b) 19 N.

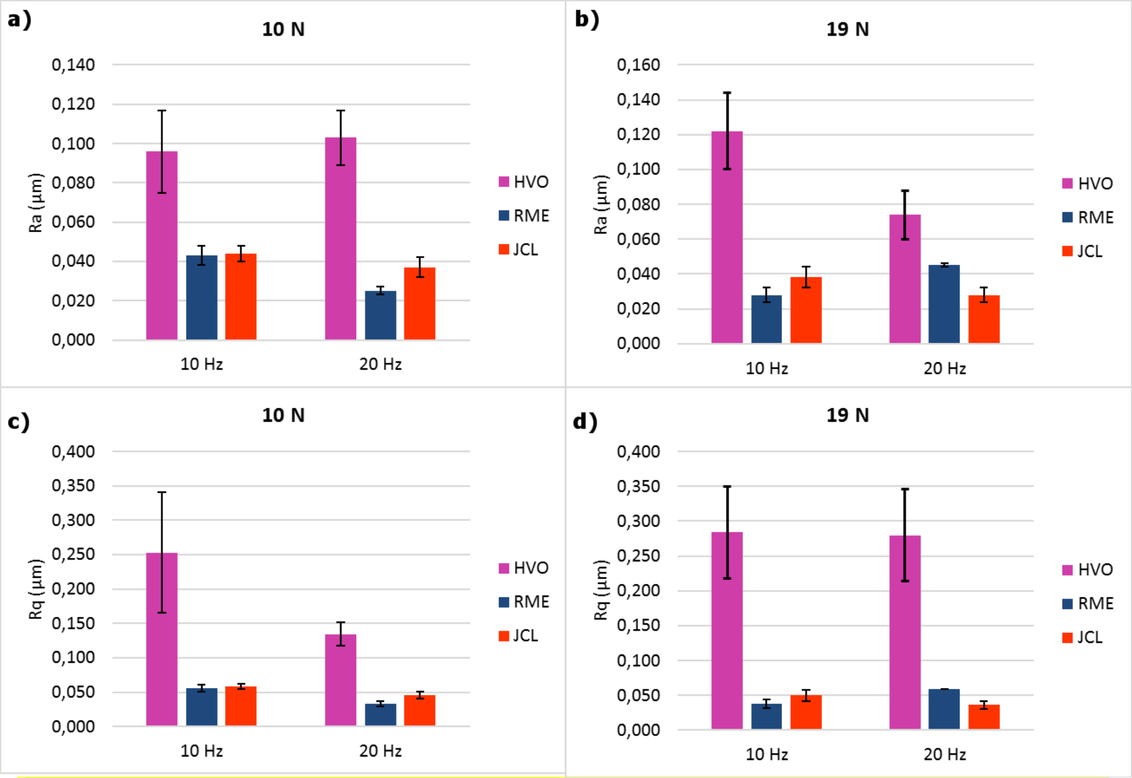

Figure 12: Surface roughness of the worn spheres after tribotests. a) and b) show the Ra values under 10 N and 19 N respectively. c) and d) show the Rq values under 10 N and 19 N.

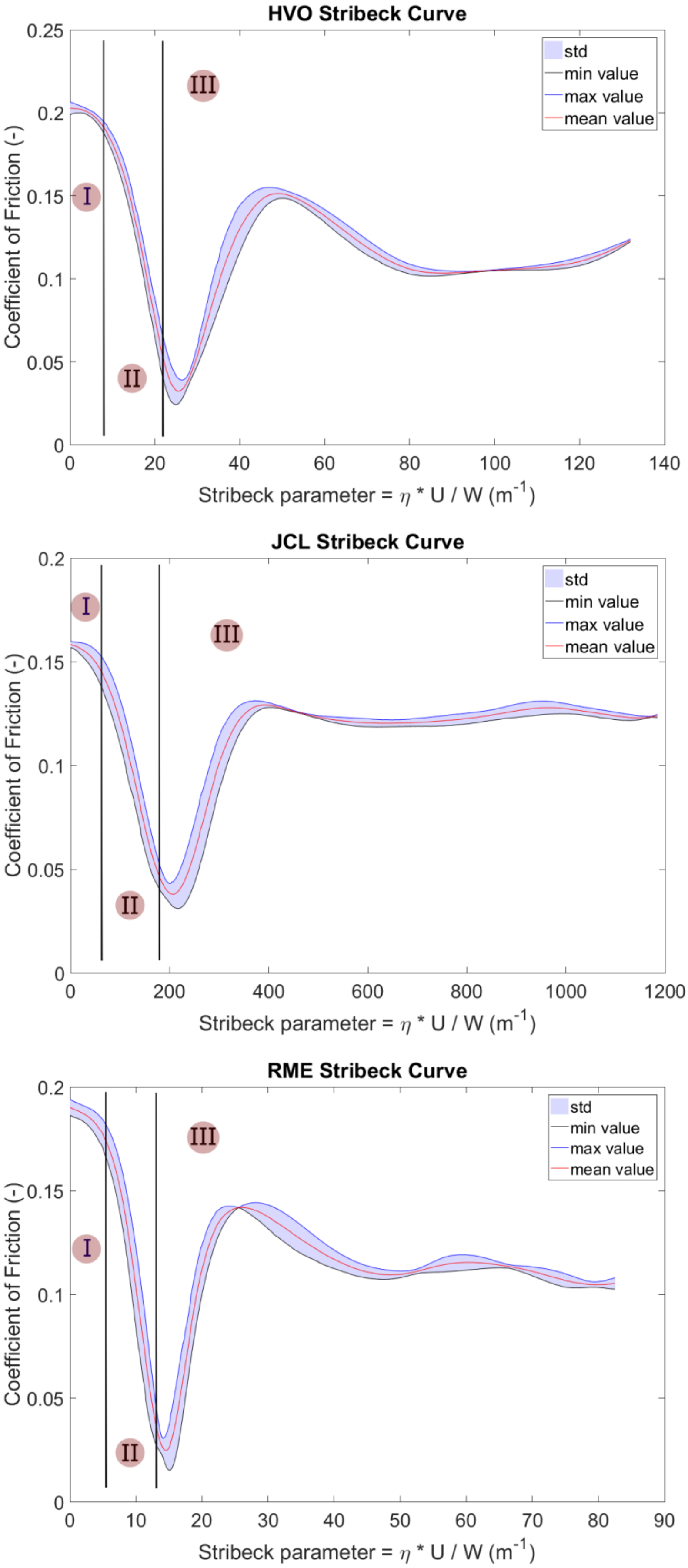

Figure 13: Stribeck curves for HVO, JCL and RME respectively.

TABLES

Table 1: Physicochemical properties of three oils.

Properties	RME	HVO	Jatropha Curcas L. oil
Density at 15ºC (kg/m^3)	884.5	780.7	916.9
Kinematic viscosity at 40ºC (cSt)	2.829	4.679	36.605
Flash point at 760 mmHg (ºC)	234±0.5	245±0.5	263±0.5
TAN (mg KOH/g)	0.22	0.08	21.4

Table 2: Wear volume and impression diameter of the worn AISI E52100 spheres after tribotests with three lubricants

		10N			19N		
		d_m (mm)	std	V (mm^3)	d_m (mm)	std	V (mm^3)
HVO	10 Hz	0,460	0,0066	0,00043	0,558	0,0068	0,00091
	20 Hz	0,474	0,0056	0,00049	0,557	0,0063	0,00092
JCL	10 Hz	0,576	0,0053	0,00098	0,739	0,0127	0,00283
	20 Hz	0,607	0,0109	0,00126	1,010	0,0086	0,01054
RME	10 Hz	0,611	0,0026	0,00138	0,685	0,0057	0,00223
	20 Hz	0,651	0,0093	0,00176	0,946	0,0068	0,00782