UDC 621.8
DOI: 10.15587/1729-4061.2024.310526

INFLUENCE OF FATTY ACID COMPOSITION ON CONTACT ANGLE AND WEAR RATE OF JATROPHA CURCAS AND SUNFLOWER'S MIXTURE BY VARYING COMPOSITIONS MIXTURE

Moch. Syamsul Ma'arif
Corresponding author
Master of Mechanical Engineering
Mechanical Engineering Doctorate Program*
E-mail: syamsulm@ub.ac.id
I Nyoman Gede Wardana
Doctor of Philosophy in Mechanical Engineering, Professor*
Djarot B. Darmadi
Doctor of Philosophy in Mechanical Engineering, Professor*
Oyong Novareza
Doctor of Philosophy in Mechanical Engineering,
Head of Professional Engineer Program
Department of Industrial Engineering**
Nanu Admantara
Bachelor of Mechanical Engineering*
Iis Siti Aisyah
Doctor of Philosophy in Mechanical Engineering, Head of Mechanical Engineering Program
Department of Mechanical Engineering
University of Muhammadiyah Malang
Raya Tlogomas str., 246, Malang, Indonesia, 65144
*Department of Mechanical Engineering**
**Brawijaya University
MT. Haryono str., 167, Malang, Indonesia, 65145

United Nation Sustainable Development Goals make sustainability become common goals which drives into investments of innovative product and technology focusing on sustainability. Cutting oils are generally made from mineral oil and the renewable replacement is sought after and one of them are Jatropha curcas and sunflower oil or blend of them. Viscosity and adsorption will influence the properties of cutting oil. The study concern on the relationship between percentage of JCO in the mixture to anti-wear properties and contact angle measured using goniometer contact angle and pin-on-disk tribometer by varying percentage of Jatropha curcas oil in mixtures for 2.5 %, 5 %, 10 %, 20 %, and 30 %. Also, molecular simulation is conducted through molecular dynamic in search of dipole moment, electrostatic potential, polarizability and bond energy. The approach is employed to connect molecular interaction and non-linearity trending of experiment. The experiment shows contact angle and wear scar width and also wear rate become higher when percentage of Jatropha curcas oil is higher. The lowest contact angle is 26.9 deg. and the highest is 36.9 deg. of 2.5 % and 30 % Jatropha oil. The highest wear rate is 6.77e-7 and the lowest is 2.74e-7 of 2.5 % and 30 % Jatropha oil. The simulation gives supporting basis in the finding of experiment in which the viscosity is more prominent in governing wear rate than adsorption. Increases of Jatropha curcas percentages have inversely proportional to dipole moment, polarizability, electrostatic potential and bonding which explain why the fatty acids become more adhere to the fatty acid than to surface. The finding is restricted only for idealized conditions both of molecular structure and surface

***Keywords:** wear rate, contact angle, molecular simulation, Jatropha curcas Linn. oil, sunflower oil*

Received date 24.07.2024
Accepted date 30.09.2024
Published date 30.10.2024

***How to Cite:** Ma'arif, M. S., Wardana, I. N. G., Darmadi, D. B., Novareza, O., Admantara, N., Aisyah, I. S. (2024). Influence of fatty acid composition on contact angle and wear rate of jatropha curcas and sunflower's mixture by varying compositions mixture. Eastern-European Journal of Enterprise Technologies, 5 (6 (131)), 15–25. https://doi.org/10.15587/1729-4061.2024.310526*

1. Introduction

The implementation of United Nations UN Sustainable Development Goals (SDGs) worldwide make sustainability become common goals in industries and equipment sector. In petroleum industries, the impact on environment by consumption of fossil fuel-based energy become severe and together with scarcity and insecurity of fossil fuel deposits lead to production and utilization of alternative energy resources. The other type of petroleum derivative is lubricants, even though it emits CO_2 very much less than its counterparts, i. e. fossil fuel, but it still needs to be substitute by more environmentally friendly lubricants [1]. The market size of lubricants worldwide annually is sizable with only a small fraction of the size is bio-based one. For more specific product, i. e. Metal Working Fluids (MWF), also have similar trends. MWF can be categorized into cutting fluid and cutting oil. Both have similarity in their basics element which constitute of base liquids (oils) and additives.

Cutting fluid in general composed from a base oil that can be constituted from mineral, synthetic, or vegetables oil. Almost 85 % of the cutting fluids are mineral-oil based [2].

In literatures, this type of lubricants may use Jatropha curcas (JCO), palm oil, jojoba, castor, soybean, peanut, maize, rapeseed, palm, and sunflower (SFO). In general, the direction of application and research in biodegradable lubricants lies in the hands of society and scholars. While society pursues on the more use of biodegradable lubricants, the scholars are concentrating their research on searching the most potential vegetable oil to replace mineral oil-based lubricants. For reasons of biodegradability, renewability, and low toxicity compared to mineral oil, those vegetable oils are increasingly being used as a base fluid in MFW. To improve the properties of vegetable oil such as enhancing their thermal stability, reducing their viscosity, and improving their lubricity, the researcher work on those vegetable oil in order to be more suitable as MWF [3].

On application of vegetable oil as MWF, the most common approach is using certain vegetable oil as base oil. Another approach is using mixed of vegetable oil with aims to improve properties of vegetable oil by balancing with low viscosity or high viscosity one. The examples are mixing castor oil with soybean oil, JCO with jojoba oil or even mixing mineral based oil with vegetable oil.

While the mixtures can be from any vegetable oils, the choice may follow certain consideration. In Indonesia, research on JCO is still pursued in effort to provide an alternative energy or lubricants. It started in early 2000s when Indonesia government initiated the program to cultivated Jatropha curcas. Another source of vegetable oil in Indonesia is palm oil. It is abundance but facing environmental issue in its cultivation. Currently in the world, renewable oil for energy and lubricants come from edible oil which constitutes 95 % such as rapeseed oil (84 %), SFO (13 %), palm oil (1 %), soybean oil, and others (2 %) [4]. In Indonesia, rapeseed oil is scarce but SFO become sixth most produce oil after palm oil, coconut, soybean, ground nut, and maize-germ oil. Therefore, research related to JCO and SFO or mixed of them become relevant to pursue to provide alternative environmentally friendly lubricant.

2. Literature review and problem statement

Cutting oils are generally made from mixtures of mineral oil and vegetable, animal or marine oil. Empirically, it has been well recognized that applying lubricants to the vicinity of the contact between tool and workpiece facilitate good machining operations. They are used to prolong tool life by decreasing tool wear, reducing cutting resistance, providing finer surface finish thus increasing machining accuracy. At higher cutting speed, since the tool wears is caused by increased temperature which lead to thermal softening then it is important that cutting fluid acts as coolant. At lower cutting speed, the lubricating function of cutting fluid is more prominent than cooling one. Another advantage when using lubricants is to protect ferrous materials against corrosion while they are awaiting further machining or assembly operation [5]. However, the corrosion inhibitor used in this research is extract of Jatropha curcas and Hibiscus sabdariffa (Rosella) which need additional process to prepare the extract even though it may use JCO directly as lubricants and also as corrosion inhibitors. Apart from being applied as lubricants, Jatropha curcas is also an effective corrosion inhibitor because of its capability in forming effective film on surface of metal against corrosion attacks. Polar functional molecules on Jatropha curcas develops barrier which acts as protective layer. This feature is governed by the difference between residual charge on metal surface and chemical structure of inhibitors. Since many advantages when using biolubricants, therefore applying lubricants in metal cutting process is advantageous.

Even though vegetable oil is an evitable replacement for mineral oil, but it has lacks of oxidation stability, extreme pressure, and anti-wear properties. Also, psychochemical characteristics and the method's application mechanism to improve properties of vegetable oil are not fully understood. In general, it is understood that cooling and lubricating properties of vegetable oil is much influenced by several factors. Those factors can be divided into:

1) substrate in which lubricants works;

2) environmental condition like humidity which may govern the forming of lubricant's layer on substrate;

3) molecular structure such as unsaturation degree, density, chain length;

4) film thickness;

5) physical properties of lubricant such as viscosity and surface tension.

Knowledge on them become key factor to achieve better lubricating performance of vegetable oil [6]. Physicochemical characteristics of vegetable oils and also mechanism to improve cooling and lubricating properties are not fully understood. This partially is caused by not many studies which comprehensively conducting study both from experimental and simulation. Also, physicochemical properties of different vegetables oils are different therefore when mapping laws of physical and chemical properties under various working conditions are still unclear. Its means when certain vegetables oil is modified then the working laws need to be examined.

Adsorption mechanism may differ when substrate and working environment is different. Substrate such as iron-based one when in humid environment may has oxide layer on the surface. Different substrate for example aluminium based or copper-based also produce different oxide layer when expose to humid environment. Interaction between carboxylic acid head group and substrate can occurs in monodentate binding mode, asymmetric doublet, and bidentate bonding mode. Chemisorption on substrate is only dependent on the interaction between the head group of fatty acid and the substrate. It is not dependent on the molecular structure of fatty acid whether saturated or unsaturated alkyl chain. In other hand, in physisorption, the layer of fatty acid above chemisorption increase with the degree of unsaturation in fatty acids and also increase the friction as well. For the chain length, increasing chain length of carboxylic acid will lead to closer molecular packing and make adsorbed film became stronger with higher lateral cohesive forces. This condition offers lower friction coefficient and higher contact angle. When film thickness increase, the coefficient of friction decreases so that more effective lubrication occurs.

Viscosity of vegetable oil is positively in relations with the amount of mono-unsaturated fatty acids but negatively in relation with the amount of poly-unsaturated fatty acid. The viscosity together with the adhesion caused by irregular intermolecular movement can be used to measure flow resistance of vegetable oil. Viscosity become an important factor since it will influence the MWF properties. Higher the MWF viscosity will make lubrications performance become more effective, but the cooling performance of lubricants and also removal of solid particles become less effective. When the viscosity is lower, it may lead to a lack of lubrication between tool edge and work piece, so does the thickness of liquid film. Poor surface quality and tool wear can occur increasingly. In machining process, therefore, a balance between fastest machining parameters and best surface quality is needed.

High viscosity lubricants will form a lubrication film that providing excellent wear protection. This protection is more effective when used at higher temperature than lower viscosity one. But high viscosity lubricants also have disadvantages in causing churning losses and excessive heat generation from fiction between the molecules. The high viscosity lubricant also hinders spreading of lubricant therefore limits lubricants flow into lubricant needed-surface. The high viscosity lubricants also consume high energy because it very resistant to the flow [7]. The difficulties arise when supplying lubricants from vegetable oil is its properties and composition are heavily dependent on the type of feedstock. In nature, vegetable oils have a relatively high viscosity but vegetable oil has different quality therefore thorough assessment of biolubricants formulation need to be performed. Low viscosity lubricant may move freely to the surface which need lubrications and will increase the ability of the oil to cool, clean and lubricate at wider range of temperature. But low viscosity lubricants cause wear and friction which generate heat because the lubricant film is not strong enough to separate two surfaces in friction. When heat generated, it even led to more friction and wear and causing accelerated wear which shorten machine/component life and also the lubricant life [8]. The study had been done on the test bed of engine using mineral oil. Very rare vegetable oils are tested on real condition test bed since cooling and lubricating properties of vegetables oil usually difficult to standardize. Also, it is unusual for vegetable oil to have low viscosity. Both studies suggest that using too low viscosity of lubricants is not recommended because it have detrimental effects related to worsened wear and even loss of some components because of heated lubricant. It leads to practices in using reasonably higher viscosity for lubricating purpose and stable molecular structure not easy to oxidize.

In literature, both of crude JCO and chemically modified JCO [9] has been investigated to be a decent candidate to replace mineral oil. Chemically modified JCO has been characterized (FTIR, GC, and NMR), tested of the properties (cloud point, pour point, and oxidative stability), assessment of tribological performance (frictional force and coefficient of friction, wear scar, and surface roughness). The study concludes that JCO is a potent biolubricant in boundary lubrication regimes with lower frictional force, coefficient of friction and wear scar diameter under different operating conditions. But again, since the composition and properties of vegetable oil is varied then research still need to be conducted when the oil come from different sources. Even though both crude and modified JCO able to provide good lubricity but the latter offers better oxidative stability, lower viscosity, and lower temperature properties. The main difference is the amount of double bonds and acyl and alkoxy functional groups in unmodified JCO which can easily react with others such as other functional groups and hydrogen which may alter their molecular composition. Therefore, it is considered more suitable as lubricants. SFO also has been studied sometimes mixtures with nano-additives. When used as lubricants, the SFO with addition of Halloysite Clay Nanotubes able to decrease coefficient of friction and wear volume loss up to 70 % [10]. In many occasion, nano-additives have been employed as anti-friction additive for many vegetable oil. Even though these approaches are not directly related to improve several drawbacks found in vegetable oils as mentioned before, but it improves sliding contact condition hence improving anti-friction properties. In this study, tribological performance of sunflower nanolubricants varied as a function of contact pressure which may led to reduction of lubricant film thickness therefore limits the process parameters which can be applied in industrial application. Therefore, optimal concentration of HNT in sunflower in accordance with certain contact pressure need to be further researched.

In general, lubricants from vegetables oil give acceptable coefficient of friction (c.o.f) for machining processes application in range of 0.3–0.45. When comparing the lubricating performance between JCO and SFO for example for grinding application by MQL, JCO give better c.o.f than SFO by 0.30 to 0.34 with specific grinding energy of 73.47 to 86.54 [11]. This research only concentrated on the experimental results of lubricating performance and not try to dig deeper on the mechanism of vegetable oil to lubricate better than the liquid paraffin oil as benchmark. Using vegetable oils as MWF in grinding process shows that vegetable oil is better applied in MQL than flooding one. In higher cutting speed, the cooling properties as given by mist of water based MWF is superior than flooding in removing the heat and lowering friction in the process. JCO has better lubrication than SFO because of more contents of unsaturated fatty acids which leads to formation of uncompact structure but more adsorption of fatty acid into metal surface. Even though JCO has superior performance than SFO, but from the production capacity it can't cope with SFO. Another problem when using JCO as lubricant is this type of oil is toxic. This condition lead to practice to add JCO to other vegetable oil when applied as lubricants in hope it still offers good lubricity while retains good spreading of lower viscosity than pure JCO as in SFO. But, work on combining between JCO and SFO as biolubricants is scarcely available in literature.

In study on vegetable oils, there are some different conclusion on the results such as on anti-wear performance. Studies on mixture of JCO and engine oil (EO) give conclusions that in most of studies the anti-wear performance of JCO is lower than EO while some results give contrary one [12]. Since anti-wear properties is much depends on materials and methods, then toe-to-toe comparison between each research is challenging and need comprehensive analysis. The explanation of this phenomenon is the additive in the EO is counter-productive since they compete each other in reaching the surface of metal, while in JCO no such competition occurs. At several papers, mixture between JCO as additive and EO also give non linearity on c.o.f's data in which for addition of JCO in range of 0–100 % the c.o.f trend is represented by polynomial trend line [13]. Since it mixture between EO and JCO, not vegetable oil to vegetable oil, then the objective to replace vegetable oil is limited. The choice is justified since EO has standard performance while JCO still need to be explore more. Additives in EO is good in reducing wear damage while JCO has better lubrication properties. The papers don't explore further about the finding and only focused on the discussion on tribometer results. Even though it is an interesting topic to explore, but very rare paper which pursue the exploration. To find the answer on those trend, further examination using such integrated in-situ adsorption measurement which combining friction, adsorption and XPS measurement may be employed. But such sophisticated test-bed is very expensive to provide.

Molecular simulation, as cheaper solution, on the study of adsorption of vegetable oil on metal surface can be found in literature even though its mainly on the adsorption or adhesion or certain additives of lubricants. Adsorption of silica nanoparticles immersed in fatty acid on alumina is studied [14]. The research is using simulation to give insight on interaction between fatty acid and the surface through molecular dynamic. This type of simulation only gives the behavior of fatty acid when expose to surface but didn't give a clue on what parameters govern the mechanism of adsorption. The study provides new insight on the relationship between structure and properties of fatty to adsorption on alumina when nanoparticles present especially on stability of foam. The counterions effect on the adsorption and morphological state of fatty acid on surface of nano-particles are largely unknown because of complexity of the interaction between nano particles, counterions, and fatty acid molecules in solution. But using simulation, interactions between fatty acid and nanoparticles can be shown changing when the concentration of counterions increase. From the molecular simulation, it is obvious than the simulation can be used to give insight into what happened in the interface between surface and lubricant's molecule but only handful of study which combine them.

3. The aim and objectives of the study

The aim of the study is to examine lubricating performance by measuring contact angle and wear rate of mixture between SFO and JCO with variation of JCO's percentage of 2.5 %, 5 %, 10 %, 20 %, and 30 % on low carbon steel and conducting simulation of molecular simulation between lubricant and surface to obtain properties and condition on the surface caused by molecular interaction between JCO and SFO mixture to surface when the composition of JCO are varied.

To achieve the aim, the following objectives are accomplished:

– conducting experiment on the mixtures of JCO and SFO with various percentage on low carbon steel so that the influence of fatty acid composition on contact angle and wear rate can be obtained by using goniometer contact angle and tribometer pin-on-disk and then evaluate the trend of contact angle and wear rate;

– adopting molecular simulation to obtain key parameters (dipole moments, polarizability, electrostatic potentials and bonding energy) in effort to explain the trends of contact angle and wear rate when the composition of JCO and SFO is varied.

4. Materials and methods

4. 1. Object and hypothesis of the study

The object of the study is contact angle and wear rate of mixture of JCO and SFO from experimental view and conducts simulation to give basic understanding on the role of molecular properties on contact angle of vegetable oils mixture on iron surface and the correlation with its wear properties. The study is based on the theory that composition of fatty acid especially type of unsaturated one will govern the viscosity hence contact angle. The viscosity in turn will influence the lubricating properties and ability of the fatty acid to protect surface of specimens against pin by forming layer. JCO has higher concentration of longer chain length of fatty acid than SFO, therefore higher concentration of JCO will form stronger layer. It makes the lubricating properties become better. Also, higher percentage of JCO will contribute to higher concentration of mono-unsaturated fatty acid in which positively related to viscosity. When poly-unsaturated fatty acid also present, but it is not significantly higher than mono-unsaturated fatty acid the previous will dictate the viscosity of mixed vegetable. When the wear rate and/or contact angle is not give a linier trending, then parameter of intermolecular interaction from simulation, especially dipole moments and polarizability will be used to explain the trending.

In this study, the assumption of surface has been made to use iron surface based on ideal BCC one and the fatty acid ones is build based on ideal structure on database as can be found in literature. Also, the simplification on the surface of iron is used. In which real-world pure iron always has oxide on it, but for the sake of calculation power of the computer the oxide is not considered present.

The molecular dynamic is a decent method when studying interaction of molecules under certain condition to simulate how each molecule behave when put on the surface of metal. The free surface energy on the metal together with the charge of molecules will make the molecules to self-organize toward lowest energy which will represent adsorption mechanisms of fatty acid into iron surface. Also, from this methods, parameters of intermolecular properties such as electrostatic potential, dipole moment, polarizability, and bonding energy will be acquired. In studying wear rate and contact angle, tribometer pin-on-disk and goniometer contact angle is a standard for measuring those parameters.

4. 2. Molecular dynamics of lubricants

Bio-lubricants are composed from Free Fatty Acids (FFA) both saturated and unsaturated ones. For plant oils, it composed mostly of triacylglycerol which contains different fatty acids attached to a single glycerol molecule. For simulation purpose, it is either treated as single fatty acid or in form of triacylglycerol one. For adsorption mechanism simulation, most of them use single fatty acid one to represent. In literatures, several parameters such as Highest Occupied Molecular Orbital-Lowest Unoccupied Molecular Orbital (HOMOs-LUMOs), electrostatic potential, dipole moment and polarizability become descriptor of the global reactivity of adsorbate to adsorbent [15].

4. 2. 1. Molecular dynamic model and energy function

The molecular model of JCO and SFO as lubricating oil was constructed in molecular simulation software. Both oils have different composition of fatty acids. Theoretically, JCO is composed of oleic acid (18:1) ($C_{18}H_{34}O_2$) of 44.7 %, linoleic acid (18:2) ($C_{18}H_{32}O_2$) of 32.8 %, palmitic acid (16:0) ($C_{16}H_{32}O_2$) of 14.2 %, stearic acid (18:0) ($C_{18}H_{36}O_2$) of 7.0 %, palmitoleic acid (16:1) ($C_{16}H_{30}O_2$) of 0.7 %, linolenic acid (18:3) ($C_{18}H_{30}O_2$) of 0.2 %, arachidic acid (20:0) ($C_{20}H_{40}O_2$) of 0.2 %, margaric 17:0 ($C_{17}H_{34}O_2$) of 0.1 %, and myristic acid ($C_{14}H_{28}O_2$) of 0.1 %. Meanwhile, SFO has composition of oleic acid (18:1) ($C_{18}H_{34}O_2$) of 15.4 %, linoleic acid (18:2) ($C_{18}H_{32}O_2$) of 2.4 %, palmitic acid (16:0) ($C_{16}H_{32}O_2$) of 8.4 %, stearic acid (18:0) ($C_{18}H_{36}O_2$) of 2.4 %, arachidic acid (20:0) ($C_{20}H_{40}O_2$) of

0.1 %, myristic acid (14:0) ($C_{14}H_{28}O_2$) of 16.3 %, caproic acid (6:0) ($C_6H_{12}O_2$) of 0.2 %, caprylic acid (8:0) ($C_8H_{16}O_2$) of 3.3 %, lauric acid (12:0) ($C_{12}H_{24}O_2$) of 47.8 %, and capric acid (10:0) ($C_{10}H_{20}O_2$) of 3.5 % [16].

In order to calculate dipole moment and bond energy of adsorbed fatty acid, the first step is to draw the molecules of fatty acid then do optimization. The second step is to calculate HOMO and LUMO of simulated fatty acid. This second step is useful to either in knowing the ΔE as energy gap between HOMO and LUMO and also to find most suitable location in fatty acid molecular chain to arrange fatty acid on surface. After the location is known then step three is executed either to calculate dipole moment and bond energy of individual fatty acid or mixture of JCO and SFO. These steps are depicted in Fig. 1.

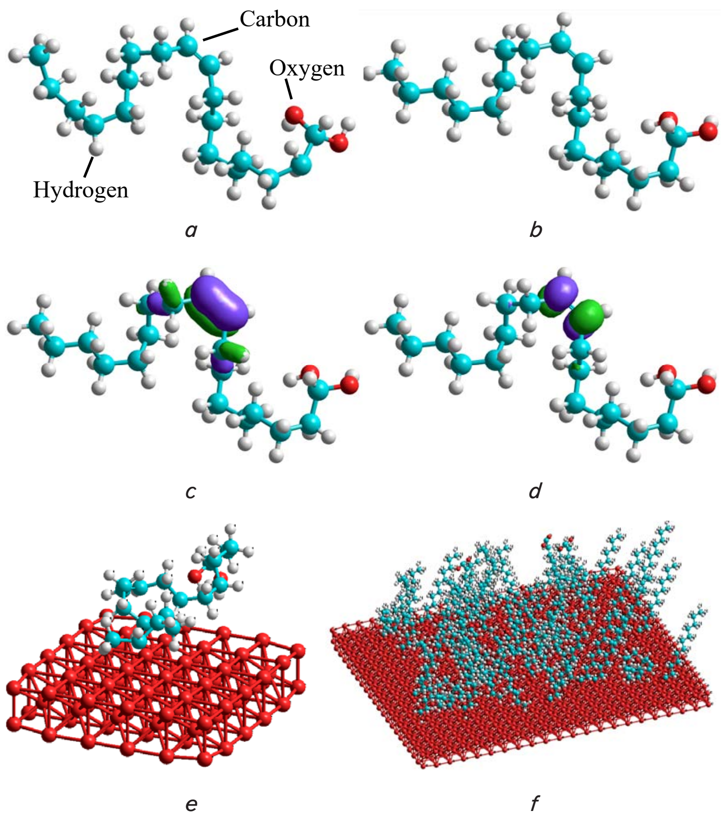


Fig. 1. Steps in simulation of fatty acid mechanism on surface: *a* – draw of oleic acid; *b* – geometrically optimized oleic acid; *c* – plotting Highest Occupied Molecular Orbital plot of oleic acid; *d* – plotting Lowest Unoccupied Molecular Orbital plot of oleic acid; *e* – calculating molecular interaction of oleic acid; *f* – calculating molecular interaction of mixture of Jatropha curcas oil and Sunflower oil

The step on e and f take different approach by observing the HOMO and LUMO. When the most active section of molecules is known, by plotting HOMO and LUMO, then the position of HOMO and LUMO is used as basis for each molecule to oriented to surface as contrary with other work which usually take the approach by using random orientation.

4. 2. 2. Simulation and calculation process

The process of simulating molecular interactions using simulation software is carried out using a computer with adequate specifications with processor using Intel Core i7 3.4 GHz and RAM DDR4 64 GB. In simple terms, the molecular mechanics and dynamic simulation process uses a very straightforward approach. If the positions of all the atoms that form a system of molecules or groups of molecules that interact with each other are known, the forces experienced by an atom can be calculated as a result of its interactions with other atoms.

For simulation purposes, both oils are represented by their constituent fatty acid components. These fatty acids have a molecular structure which is represented by an image so that in the software it is converted into a number. The computation begins by drawing the chemical structure of the lubricant components. This chemical structure represents how atoms bond in a three-dimensional plane in the most optimal structural form. This optimal value is represented by the computational state of molecular mechanics through iteration until it reaches a state where small changes in bond angles and stretching do not cause too sharp changes in the energy. The stopping point for the iteration is defined as the Root Mean Square (RMS) parameter. Convergence is sought using the Polak-Ribiere (conjugate gradient) methods. To obtain other parameters such as dipole moment, bond energy, etc., molecular mechanics methods such as MM+ method can be used which provides more speed in terms of calculations even though the results are less accurate than DFT. Furthermore, after the fatty acid molecule is drawn, the parameters you want to look for such as molecular energy and dipole moment, and others are obtained.

To determine the adsorption of each fatty acid component, parameters such as dipole moment, E_{HOMO}, E_{LUMO}, bond energy and heat of bond formation are used as the basis for determining the level of adsorption. In general, the molecular orbital energy level expressed in Highest Occupied Molecular Orbital (HOMO) and Lowest Un-occupied Molecular Orbital (LUMO) will express the adsorption level of each fatty acid that forms JCO and VCO. To calculate HOMO+ and LUMO-, the semi-empirical MINDO/3 method is used, which is available in commercial computer programs.

4. 3. Adsorption, viscosity and lubricity

Effectivity of lubricants is well described by its properties. Two of them are wetting and lubricating properties. Wetting property is influenced by the balance between adhesive forces (attraction between the liquid and the solid surface) and cohesive forces (attraction within the liquid molecules). In simulation, the wetting property usually is represented by contact angle simulation, adsorption mechanism simulation, and molecular interaction by computing electrostatic potential and bond energy in adsorption process. In this paper, the molecular interaction methods are chosen.

Table 1 depict composition of fatty acids in mol per liter of mixture of JCO and SFO for simulation. Depending on the hardware, i. e. capacity of computing power, it is more time consuming to do simulation using full range of values given in the tables. Therefore, for computing power consideration, the amount of molecules involves in simulation is need to be considered wisely.

In this calculation, maximum of 45 fatty acid molecules and certain size of iron is employed. Using stearic acid as benchmark the for example for 0 % of JCO, the molecules involved in simulation are 6 molecules of oleic acid, 1 molecule of linoleic acid, 4 molecules of palmitic acid, 1 molecule of stearic acid, 7 molecules of myristic acid, 1 molecule of caprylic acid, 20 molecules of lauric acid and 12 molecules of capric acid.

Table 1

Composition of fatty acid of JCO in mixture of JCO + SFO (mol) for simulation

Fatty Acid	Percentage of JCO in Mixture of JCO+SFO (%)					
	0	2.5	5	15	20	30
Oleic acid (18:1)	6.42	6.72	7.03	7.64	8.86	10.08
Linoleic acid (18:2)	1.00	1.32	1.63	2.27	3.53	4.80
Palmitic acid (16:0)	3.50	3.56	3.62	3.74	3.98	4.23
Stearic acid (18:0)	1.00	1.05	1.10	1.19	1.38	1.58
Palmitoleic acid (16:1)	0.00	0.01	0.01	0.03	0.06	0.09
Linolenic acid (18:3)	0.00	0.00	0.00	0.01	0.02	0.03
Arachidic acid (20:0)	0.08	0.08	0.08	0.08	0.08	0.08
Margaric acid (17:0)	0.00	0.00	0.00	0.00	0.01	0.01
Myristic acid (14:0)	6.79	6.62	6.45	6.12	5.44	4.77
Caproic acid (6:0)	0.13	0.12	0.12	0.11	0.10	0.09
Caprylic acid (8:0)	1.38	1.34	1.31	1.24	1.10	0.96
Lauric acid (12:0)	19.92	19.42	18.92	17.93	15.93	13.94
Capric acid (10:0)	1.46	1.42	1.39	1.31	1.17	1.02

4. 4. Experimental procedures

Tribology test. The material for the test is given in Fig. 2. Tribology tests were carried out using pin-on-disk apparatus. The apparatus is an in-house one (Fig. 2, *a*). The diameter of the pin is 4 mm with a nose radius of 0.3 mm. Meanwhile, the specimen used in this research is low carbon steel. This type of steel has specification as in Table 2.

a *b* *c*

Fig. 2. Tribology test: *a* – in-house pin-on-disk apparatus; *b* – specimen after test; *c* – scale

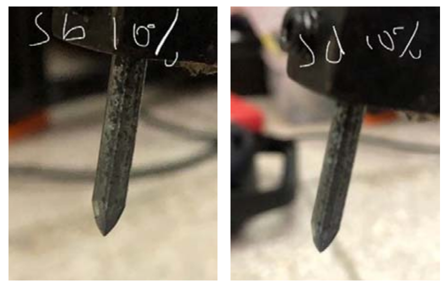
Table 2

Specification of material

Specimen	Hardness (HV)	Surface Roughness (mm)
Low carbon steel	145	0.451

The wear test apparatus makes the specimen to move around the center of the disc while the pin is in a stationary position. The pin was pressed against the specimen by applying a force of 500 grams weight mounted on the swing arm above the pin. The specimen was prepared by cutting a low steel bar with φ 32 mm and a thickness of 8 mm (Fig. 2, *b*). The specimen was then sanded to meet the requirement of surface roughness under Ra=0.8 μm. The vegetable oils used in this research are JCO (Fig. 2, *c*) and SFO (Fig. 2, *d*). The JCO used is the oil from variety of Jatropha curcas Linn. cultivated by the UMM research team under the name JCUMM5, while the SFO used is one which is commercially available.

For the wear test, the rotational speed of the driving motor is regulated by applying a voltage of 12V and the rotation is measured using a tachometer. To determine the weight loss due to friction with the pin, before carrying out the tribology test the specimen was weighed with a digital scale which has an accuracy of up to 0.0001 grams (Fig. 2, *e*). Weighing is also carried out after tribological tests are conducted. To determine the condition of the pin tip, before and after the tribological test the pin is photographed to find out how worn the tip (radius) of the pin is (Fig. 3). To keep the specimen clean, before and after measuring or weighing, the specimen is cleaned and dried.



a *b*

Fig. 3. Pin condition: *a* – before (sb 10 %); *b* – after (sb 10 %) certain wear test run

From Fig. 3, it is shown that pin radius doesn't experience significant wear between before test (Fig. 3, *a*) and after test (Fig. 3, *b*). Wear is measured in two ways, which is by the principle of volume loss due to wear tests and mass loss. The first method is carried out using (1) with the assumption that the pin does not experience significant wear [17]:

$$\text{disk volume lost, mm}^3 = \frac{\pi(\text{wear track radius, mm})(\text{wear scar diameter, mm})^3}{6(\text{sphere radius, mm})}. \quad (1)$$

Meanwhile, the second method is conducted by using (2):

$$\text{volume lost, mm}^3 = \frac{\text{mass loss, g}}{\text{density, g/cm}^3}. \quad (2)$$

Contact angle measurement of mixed bio-lubricants on low carbon steel was conducted at room temperature (25 °C) to compare their wetting performance with series camera. Generally accepted that a high contact angle indicates poor adsorption between the lubricant and surface while a low contact angle indicates good one as illustrated in Fig. 4. The contact angle measurement of mixture is captured by using apparatus as in Fig. 5.

a *b*

Fig. 4. Contact angle to determine adsorption characteristic between lubricants and surface: *a* – poor wettability; *b* – good wettability

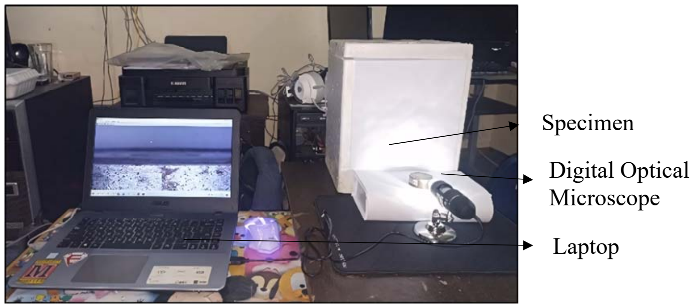


Fig. 5. Contact angle measurement apparatus

Before the measurement, low carbon steel surface was rinsed with ethanol and dried in stream of hot air. One drop of sample was dropped on the steel surface using a syringe. To make sure that steady state contact angles' value in average was obtained, a waiting period of 5 seconds was applied to allow droplet to stabilize and at least three measurement were conducted for each mixture of bio-lubricants.

5. Results of the experiment and molecular simulation of addition of Jatropha curcas oil to contact angle and wear rate of vegetable oil mixture

5. 1. Contact angle and wear rate of mixture of Jatropha curcas oil and Sunflower oil

Fig. 6 shows contact angle for different mixture of bio-lubricant as function of JCO to percentage at room temperature (25 °C). It became evident that adding of JCO into SFO will increase the contact angle and therefore the viscosity of mixture. When it is possible to use the 2.5 % of JCO as base, the next percentage, i. e. 5 % of JCO increase the contact angle at 6.7 %. For the next percentage of 10 % of JCO, the contact angle increases at 10.41 %. Percentage of 20.5 % of JCO give the increase of contact angle for 20.45 %. In a case of lowest percentage to the highest percentage of JCO, i. e. 30 %, the contact angle increases about 37.17 %.

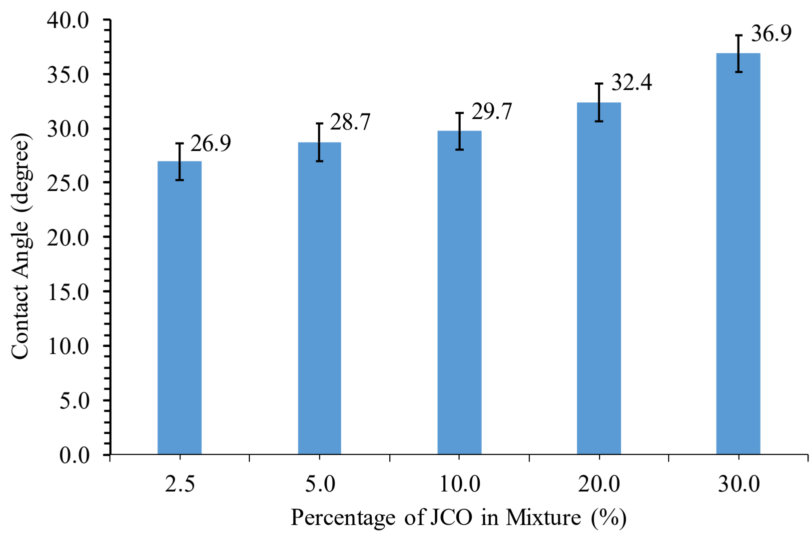


Fig. 6. Contact angle for various mixture of Jatropha curcas oil and Sunflower oil

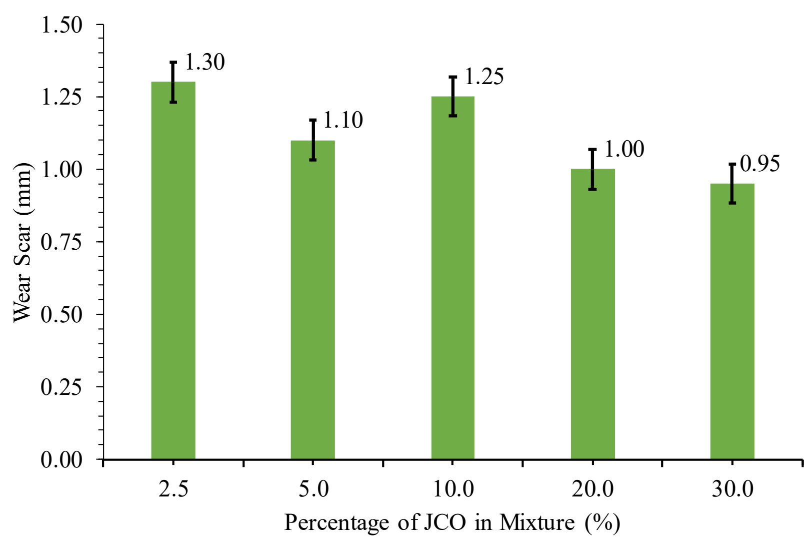


Fig. 7. Wear scar for various mixture of Jatropha curcas oil and Sunflower oil

From the wear test presented in Fig. 7, 8, it is obvious that higher percentage of JCO produce narrower wear scar. Comparing the values of wear scars for each variation, it shows 15.38 % decrease of scar's width for blending of 2.5 % and 5 %, then 13.64 % decrease for blending of 5 % and 10 %. Next, for 10 % and 20 % blend the decrease of scar's width is 20.00 % and for 20 % and 30 % blend it shows 5 % of decrease. When comparing the lowest and highest percentage of JCO content in the blend of SFO and JCO, the value is 26.92 %. From the results as mentioned before, the most significant decrease in width of scar is found for percentage blend of 5 % and 30 %.

Wear scar and wear rate of blended JCO with SFO tend to show fluctuations for range of 2.5–20 % as shown in Fig. 8.

Fig. 8 presents wear rate on low carbon steel when using lubricants from the mixture of SFO and JCO with various percentage. As seen in the figure, the wear rate becomes lower when percentage of JCO increase. When to take the basis of wear rate of 2.5 % percentage of JCO, then of 5 % of JCO the wear rate decreases 23.04 %. For 10 % of JCO percentage, the decrease is 18,32 % while of 20 % of JCO percentage, the decrease is 34.42 %. The most significant decrease is of 30 % of JCIO percentage of 59.53 %.

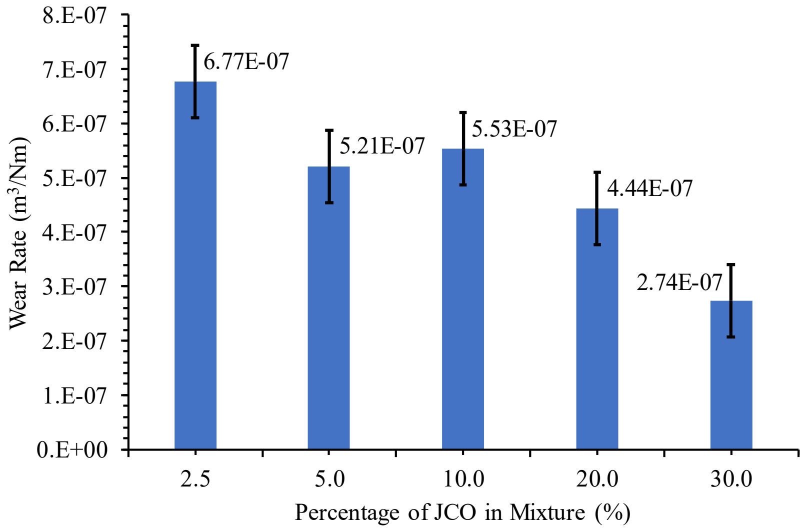


Fig. 8. Wear rate for various mixture of Jatropha curcas oil and Sunflower oil

5. 2. Value of dipole moment and polarizability

As shown in Table 3, varied percentages of JCO in the mixture give different values of molecular parameters. Adding more JCO in the mixture makes dipole moment decrease and also polarizability. Total electrostatic potential of FFA – iron alpha system become less negative when concentration of JCO is increased. Total bond energy decrease when more JCO is added to mixture.

Table 3

Dipole moment, bond energy, and heat of bond formation of fatty acids to 20x20x1 iron-alpha

Fatty Acid	Percentage of JCO in Mixture of JCO+SFO (%)					
	0	2.5	5	15	20	30
Dipole moment (debyes)	17.320	15.800	15.530	9.885	8.154	6.738
Electrostatic potential (Volts)	–43.669	–46.894	–46.427	–47.763	–3.145	–6.264
Polarizability (Å^3)	521.77	483.85	481.64	475.93	473.01	470.24
Bond (kcal/mol)	39921.300	39924.500	39913.200	39917.900	39853.000	39856.400

Dipole moment is decrease from 17.320 debyes for 0 % JCO to 15.800 debyes when JCO is 2.5 %. This trend also consistent with increase of JCO in which for 5 % then the dipole moments is 13.530 while of 15 % of JCO the dipole moments is 9.885. Dipole moment of 20 % and 30 % of JCO are 8.154 and 6.738 respectively. Other parameter, i. e. electrostatic potential for percentage of JCO 0 %, 2.5 %, 5 %, 10 %, 15 %, 20 %, and 30 % are –43.669, –46.894, –46.427, –47.763, –3.145, and –6.264 Volts respectively. The polarizability for the same percentage is 521.77, 483.85, 481.64, 475.93, 473.01, and 470.24 Å^3 respectively while for bond energy for fatty acid-iron system the value is 39921.300, 39924.500, 39913.200, 39917.900, 39853.000, and 39856.400 kcal/mol respectively.

6. Discussion of the experiment and molecular simulation of addition of Jatropha curcas oil to contact angle and wear rate of mixture of vegetable oil

When comparing contact angle for different percentage JCO in the mixture with 2.5 %, 5 %, 10 %, 15 %, 20 %, and 30 %, the contact angle is increased with value of 6.7 %, 3.5 %, 9.1 %, and 13.9 % respectively as given in Fig. 6. The results show that the contact angle measurements follow general rule of viscosity of mixed oil. It is known that viscosity of JCO is higher than viscosity of SFO, and the contact angle of each mixture represent the change of viscosity of the mixture. Higher percentage of JCO, will make the contact angle, and theoretically the viscosity, becomes higher.

The data of wear scar as shown in Fig. 7 in this research shows consistency with other researches such as for blending Extra Virgin Olive Oil (EEVO) and JCO where higher percentage of JCO will give narrower wear scars. Another research which compare the scar width of pure petroleum diesel and biodiesel with 20 % of JCO also shows similar research in which biodiesel give narrower wear scars than pure petroleum diesel. Study on trans-esterification of JCO also agreed with the research in which the trans-esterified JCO are blended with mineral oil and higher the content of JCO then the wear scar became decreasing. The data trends on the wear rate also in line with wear scar data in which higher percentage of JCO make wear rate decrease. Wear rate is governed by viscosity and adsorption of lubricants. Higher viscosity of lubricants will give good strength in film thus more efficient in preventing friction between two surfaces in contact. Higher viscosity of lubricants also gives lower adsorption to the surface. But it is not necessary to use too viscous lubricants because the sliding contact will produce heat and need more energy to move. From data of wear rate as depicted in Fig. 8 also give the trend that higher percentage of JCO will give better anti-wear performance since the wear rate is decreasing in general. Based on the result of wear test, the viscosity is dominant in governing lubrication. When to look closer to the wear scar (Fig. 7) and wear rate (Fig. 8), both give a result that for 5 % of JCO the data show slightly lower value of them than of 2.5 % and 10 %.

Performance of lubricants to reduce friction is governed mainly by viscosity of lubricants and adsorption to surface of lubricated one. The value of viscosity can be estimated from the composition of fatty acid or molecules while also give insight into adsorption behavior through molecular simulation. JCO's fatty acid is composed mainly by oleic acid (18:1), linoleic acid (18:2), and palmitic acid (16:0) while SFO's fatty acid composition is dominated by lauric acid (12:0), myristic acid (14:0), and oleic acid (18:1). While JCO is dominated by unsaturated fatty acid with longer chain, the SFO is dominated by saturated fatty acid with shorter chain. It also explains why JCO is more viscous than SFO.

Reactivity of a molecular system can be described by molecular electrostatic potential (MEP). MEP give understanding of system physicochemical properties and its relationship with molecular structure and also reactivity toward the attack of electrophilic and nucleophilic [18]. Electrostatic potential has a minor role in the adsorption, especially on hydrophilic surface. This parameter shows how structure of molecules and its reactivity. Oleic acid and linoleic acid are unsaturated fatty acid and increasing when percentage of JCO higher. Total bond energy described how weakly or strongly bond between FFA and surface.

Other parameter, i. e. dipole moments, indicates the polarity of molecular system and in general have inverse trend with adsorption energy and enthalpy of adsorption process. Meanwhile, polarizability define the state of electron cloud when interact with electric charge. High polarizability means electrons can be easily taken away from the nucleus. Also, it refers to the tendency of molecules in developing dipole moments in response to an electric field [19].

From molecular simulation, the dipole moments and polarizability become lower when percentage of JCO is increased as shown in Table 3. When dipole moment become lower the adsorption energy also become less negative [20]. Lower adsorption energy means the adsorption of mixture to surface is less than pure SFO since it can't form strong chemical interaction which makes it less stable. Table 3. shows that for 5 % of JCO there are slightly lower in electrostatic potential and bond energy value which may become the reason why the wear rate of mixture slightly lower.

Depend on the type of adsorption, whether it take form physio-adsorption or chemisorption, the mechanism of adsorption is different. For physio-adsorption, the only bonding is weak van der Waals type of force. This type of bonding doesn't change distribution of electron density both in molecules or surfaces. In chemisorption, the bonding may take form of ionic or covalent bonding with redistribution of electron density occurs in either molecules or surfaces. For mechanism of adsorption in this work tend to physio-adsorption one.

The study needs to be further explored since there are some limitation of the study. When comparing between simulation and experiment, always the simulation can't reflect actual experimental one because of it depend on the methods and initial conditions. Also, the time of simulation is conducted in very short fraction of time than experimental one because of computational power of hardware even though it is still decent way to complement the experimental research. Related to this study, further simulation which represent the lubrication condition between two surfaces which is separated by mixed vegetable lubricant need to be explore more so that the whole picture of theoretical background of the topics can be presented more comprehensively.

The study has two limitations. The experimental one is much depending on the varieties of Jatropha curcas and sunflower together with cultivated area therefore the results is valid only for JCUMM5 variety of JCO which cultivated in Pasuruan, East Java-Indonesia and SFO from certain vendor. The simulation one is represent for idealize both of fatty acid molecules and pure iron with BCC only. Other surface such as surface with oxide and others cis-fatty acid need to be run independently. Also, JCO used in the study is crude one. This type of JCO has disadvantages in oxidative stability and limits its use in practical/industrial application. Therefore, the direction of future research needs to be directed to epoxidized or esterified JCO in order to improve oxidative stability and more suitable to industrial application even though it will give more viscous and oxygen adsorption in the fatty acid chain.

7. Conclusions

1. Adding more JCO into mixture with SFO will make oil mixture become more viscous since JCO is more viscous than SFO. This is indirectly concluded from the value of contact angle in which become higher when more JCO is added. With contact angle's value of 26.9 degree to 36.9 degree then it can be associated with good wettability. Since the value of contact angle is higher for higher percentage of JCO then it inversely proportional to wettability. Addition of JCO is also influencing the wear scar and wear rate on pin-on-disc test using the mixture as lubricant. Higher percentage of JCO in mixture will make wear scar and also wear rate become lower. In general, the addition of JCO improve wear characteristic for both wear scar width and wear rate. The exception is of 5 % addition of JCO in which both wear rate and wear scar slightly lower than 2.5 % and 10 % of JCO's addition.

2. Chosen parameters of molecular simulation i. e. dipole moment, electrostatic potential, polarizability and bond energy are obtained. Increasing of percentage of JCO in mixture has inversely influence on dipole moment and polarizability in which it will decrease the value of both parameters. For dipole moments, the range of value is 17.320 debyes for 0 % of JCO to 6.338 debyes of 30 % of JCO. The decrease is about 63.4 %. Polarizability is decreasing from 521.77 Å^3 to 470.24 Å^3 of 0 % JCO to 30 % JCO. It's about 9.87 % decrease. The electrostatic potential is decreasing (less negative) when the percentage of JCO is increasing in which the electrostatic potentials is –43.669 Volts of 0 % of JCO and –3.145 Volts of 20 % JCO and about 92.79%. The bonding energy which combination of lubricant (fatty acid) and surface in general has decreasing trending. Its value decrease but fluctuate from 39921.300 kcal/mol to 39856.400 kcal/mol of 0 % JCO and 30 % JCO which about 0.16 %. From the simulation, especially from the value of dipole moments and polarizability, give explanation why the mixture become more adhere to the fatty acid than to surface hence higher viscosity and for some extent better anti-wear properties. The slight fluctuation in electrostatic potential and bond energy may explain why the wear scar and wear rate slightly lower in that percentage.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, person-

al, authorship or otherwise, that could affect the research and its results presented in this paper.

Financing

This research is partly funded through the Professor Grant Program from Faculty of Engineering, Brawijaya University of 2022 Budget Year Research Contract number: 06/UN10.F07/H.PN/2022.

Data availability

Data will be made available on reasonable request.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

Acknowledgments

The author would like to extend their deepest appreciation to the Mechanical Engineering Department of Brawijaya University and the Mechanical Engineering Department of Muhammadiyah University of Malang for their support in publishing this research.

References

1. Luna, F. M. T., Cavalcante, J. B., Silva, F. O. N., Cavalcante, C. L. (2015). Studies on biodegradability of bio-based lubricants. Tribology International, 92, 301–306. https://doi.org/10.1016/j.triboint.2015.07.007
2. Tang, L., Zhang, Y., Li, C., Zhou, Z., Nie, X., Chen, Y. et al. (2022). Biological Stability of Water-Based Cutting Fluids: Progress and Application. Chinese Journal of Mechanical Engineering, 35 (1). https://doi.org/10.1186/s10033-021-00667-z
3. Afonso, I. S., Nobrega, G., Lima, R., Gomes, J. R., Ribeiro, J. E. (2023). Conventional and Recent Advances of Vegetable Oils as Metalworking Fluids (MWFs): A Review. Lubricants, 11 (4), 160. https://doi.org/10.3390/lubricants11040160
4. Milano, J., Silitonga, A. S., Tiong, S. K., Ong, M. Y., Masudi, A., Hassan, M. H. et al. (2024). A Comprehensive exploration of jatropha curcas biodiesel production as a viable alternative feedstock in the fuel industry – Performance evaluation and feasibility analysis. Mechanical Engineering for Society and Industry, 4 (1), 17–37. https://doi.org/10.31603/mesi.10610
5. Abdul Aziz, M. A. A., Hamzah, E., Selamat, M. (2022). Performances of plant based corrosion inhibitors in controlling corrosion of mild steel in sodium chloride environment. Materials Today: Proceedings, 51, 1344–1349. https://doi.org/10.1016/j.matpr.2021.11.385
6. Zhang, X., Li, C., Zhou, Z., Liu, B., Zhang, Y., Yang, M. et al. (2023). Vegetable Oil-Based Nanolubricants in Machining: From Physicochemical Properties to Application. Chinese Journal of Mechanical Engineering, 36 (1). https://doi.org/10.1186/s10033-023-00895-5
7. Narayana Sarma, R., Vinu, R. (2022). Current Status and Future Prospects of Biolubricants: Properties and Applications. Lubricants, 10 (4), 70. https://doi.org/10.3390/lubricants10040070
8. Hermawan, A., Rahardja, I. B., Syam, M. Y., Sukismo, H., Fatah, N., Mardiono, M. (2019). Analysis of Viscosity of Lubricating Oil on Generator Machine Working Hours at KP. Macan Tutul 4203. Journal of Applied Sciences and Advanced Technology, 1 (3), 69–73. Available at: https://jurnal.umj.ac.id/index.php/JASAT/article/view/4312
9. Rajasozhaperumal, G., Kannan, C. (2023). Comparative evaluation of chemically modified Jatropha oils as sustainable biolubricants in boundary lubrication regime. Tribology International, 186, 108594. https://doi.org/10.1016/j.triboint.2023.108594
10. Biswas, M. A. S., Rahman, M. M., Ortega, J. A., Peña-Parás, L., Maldonado-Cortés, D., González, J. A. et al. (2022). Lubrication Performance of Sunflower Oil Reinforced with Halloysite Clay Nanotubes (HNT) as Lubricant Additives. Lubricants, 10 (7), 139. https://doi.org/10.3390/lubricants10070139
11. Wang, Y., Li, C., Zhang, Y., Yang, M., Li, B., Jia, D. et al. (2016). Experimental evaluation of the lubrication properties of the wheel/workpiece interface in minimum quantity lubrication (MQL) grinding using different types of vegetable oils. Journal of Cleaner Production, 127, 487–499. https://doi.org/10.1016/j.jclepro.2016.03.121
12. Woma, T. Y., Ipilakyaa, T. D., Abdullahi, A. A., Okoro, U. G., Bello, A., Abutu, J. et al. (2023). Evaluation of Friction Co-efficient and Wear Performance of Jatropha Oil Using Standard Steel Ball on Aluminium Disc Tribometer. Journal of Materials and Environmental Science, 14 (10), 1266–1277. Available at: https://www.jmaterenvironsci.com/Document/vol14/vol14_N10/JMES-2023-14108-Woma.pdf
13. Figueroa, M., García, E., Hernández, E. A. G., Vite-Torres, M. (2014). Friction and Wear of Jatropha curcas Oil Using a Four Balls Tester. Advanced Materials Research, 902, 76–81. https://doi.org/10.4028/www.scientific.net/amr.902.76
14. Ma, Y., Wu, Y., Lee, J. G., He, L., Rother, G., Fameau, A.-L. et al. (2020). Adsorption of Fatty Acid Molecules on Amine-Functionalized Silica Nanoparticles: Surface Organization and Foam Stability. Langmuir, 36 (14), 3703–3712. https://doi.org/10.1021/acs.langmuir.0c00156

15. Ma'arif, Moch. S., Wardana, I. N. G., Darmadi, D. B., Novareza, O., Abidin, Z., Sulistyo, E., Darsono, C. H. (2024). The Influence of Eugenol in Lubrication Properties of Crude Jatropha Curcas Lin. International Journal of Integrated Engineering, 16 (2). https://doi.org/10.30880/ijie.2024.16.02.017
16. Edem, D. O. (2002). Palm oil: Biochemical, physiological, nutritional, hematological and toxicological aspects: A review. Plant Foods for Human Nutrition, 57 (3/4), 319–341. https://doi.org/10.1023/a:1021828132707
17. Designation: G 99-95a (Reapproved 2000)e1. Test Method for Wear Testing with a Pin-on-Disk Apparatus. ASTM. Available at: https://cdn.standards.iteh.ai/samples/9915/022a33a120e74c24a23b628770221138/ASTM-G99-95a-2000-e1.pdf
18. Farrokhnia, M. (2020). Density Functional Theory Studies on the Antioxidant Mechanism and Electronic Properties of Some Bioactive Marine Meroterpenoids: Sargahydroquionic Acid and Sargachromanol. ACS Omega, 5 (32), 20382–20390. https://doi.org/10.1021/acsomega.0c02354
19. Cho, K. (2005). Polarizabilities. Encyclopedia of Condensed Matter Physics, 341–347. https://doi.org/10.1016/b0-12-369401-9/00603-3
20. Bibi, S., Ur-rehman, S., Khalid, L., Bhatti, I. A., Bhatti, H. N., Iqbal, J. et al. (2022). Investigation of the adsorption properties of gemcitabine anticancer drug with metal-doped boron nitride fullerenes as a drug-delivery carrier: a DFT study. RSC Advances, 12 (5), 2873–2887. https://doi.org/10.1039/d1ra09319c