

Anti-Oxidant Property of Eichhornia Crassipes In Oil Samples

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Abstract: This study on *Eichhornia Crassipes* focus on its advantageous contribution to oil sample protection through its anti-oxidant and anti-corrosion properties. It was discovered to possess antioxidant constituents of phospholipid with strong structure of amphipathic molecules with much of hydrophobic strength. *Eichhornia Crassipes* contain triglycerides known as lutein, lycopene, α -Tocopherol, zeaxanthin, astaxanthin which help in protecting lubricants against oxidation, corrosion, thermolysis and hydrolysis. These good potential helps in neutralizing acids also the chitins potential found at the root region of the plant, serves as destroyer for some dangerous contaminants in the lubricant. This function as a key quid in extending the life span of an oil lubricant degradation from occurring. However, the antioxidants still deplete in the process as a result of vigorous reactions to the formation of some acids in the system.

Keywords: Anti-oxidant, degradation, *Eichhornia Crassipes*, lubricants, and phospholipid.

I. INTRODUCTION

Degradation of oil lubricant causes series of catastrophes in the operational performance and overall output of an engine set up. Inability of lubricants to resist redox reaction, corrosion and even rust, completely affect the lubricating performance. These further lead to friction and wear, to form the most dangerous impact on engine elements. All mechanisms in machine set up involve a lot of mechanical contacts between various surfaces [1]. Wear impact shorten machine service life, causes machine malfunction and enormous losses, due to interrupted production. To minimize the impact and misadventure failure caused by oxidation/corrosion effect (friction structures), lubricants with sufficient anti-oxidants are usually introduced. In machine operation, energy losses are recorded and negatively affects machine efficiency [2].

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In support of current sustainability strive towards innovative change in a balanced environment, whereby the exploitation of resources, the phase of investments, the inclination of technological development and institutional change are compounded as the formula to enhance both current and future potential to meet human needs and aspirations. This challenges have become more critical concern in the field of tribology most especially where oxidation and corrosions are much observed like in maritime industry [3]. Though series of nanoparticles (NPs) have been studied by biomedical and nanotechnology researcher and their demand together with applications in the industrial utilization has been for past decades [4]. Notwithstanding, the toxic effect of those inorganic substances as anti-oxidants in oil samples will not be under-estimated. In addition, the resultant destructive effect of nano-toxicology had been discussed by bio-researcher with better understanding and more insights towards bio-materials that is ecological friendly [4]–[7]. Currently, major fuel and lubricants together with its additives (anti-oxidants) used by internal combustion engines are petroleum (synthetic) derived products [8]. The final product of these materials, turns to be a serious challenge to our ecosystem due to the emission of gasses especially the greenhouse gas [9], [10]. Adopting the world sustainability strive in order to combat these poisonous emissions, alternative lubricants and additives through green technology are being formulated for existing engines with or without modifications [11]. Bio-additives and lubricants have better affinity to metal surfaces in terms of tribological performance, provides better anticorrosion than petroleum derived type [4], [12], [13]. *Eichhornia Crassipes* processed compounds with some good potentials are active green substitute to toxic inorganic compound constitutes like Sulphur (S) and Phosphorus (P) based additives. It also has capacity in synergetic enhancement with conventional ZDDP and other high additives [14]. According to American Petroleum Institute (API), group 1 base oils in the line of the five groups of base oils are in decline [15][16]–[18] Mineral oil of group 11 and 111 base oils, that are more refined as well as fully synthetic polyalphaolefines (PAO) which represents group IV, can be found in an increasing number of commercial lubricant formulations [19]. Group V summarizes all of the other types of base oils such as silicones, polyalkylene glycol (PAG) ethers, phosphate esters, bio-lubes, and various synthetic esters [8], [18]. Oxidation rate as part of oil degradation, depends on quality and base oil type, as well as synergetic of additives package used. Some of well refined synthetics oil like polyalphaolefins (PAO), constitutes better oxidation stability than counterpart of mineral oils [16], [20].

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This enables the oil to resist oxidation at some higher operating temperatures thus improve oxidation stability. It concisely stated that hydro-treated base stocks class have superior oxidation resistance and thermal stability than does solvent-refined class base oil [21]. Solvent approach of refining, results in base oil production, that contain more of natural anti-oxidants of sulphur compounds. These categories of base oil retain a natural tendency to prevent oxidation, while the class of hydro-treated base oils must be providing with additional anti-oxidants for oxidation stability and thermal balancing. Many of hydro-treated base oils have very poor solubility characteristics [22]. Reason could be improper formulation, resulting in additives suspensions after blending. In the operation, immediately the anti-oxidants are depleted or weakened in defending lubricant, the oxidation of the oil might occur very rapidly [23].

II. EICHHORNIA CRASSIPES AS A SOURCE OF ANTI-OXIDANTS/CORROSION TO OIL SAMPLES

Water hyacinth with a botanical name *Eichhornia Crassipes Martius*, is a weed ubiquitously monocotyledonous plant found in rivers, lakes and other water bodies across the globe. Classified to the family potederiaceae of lily group (liliaceae), and originated from Brazil and Equador region. It bears aesthetically pleasing coloured flowers along their round to oblong curved leaves and waxy coated petioles. The growth is highly proliferation with inches to about a meter in height. To enable it float, its leaves and stem contain air filled sacs. Despite the challenges associated with the proliferation growth by blocking the water ways thereby makes navigation and other water activities difficult. The nature and growths also serves as promoters for bacteria and other water diseases. In the other hand, it further provides advantageous potentials [24]–[26] in traditional medicine, used in phytoremediation, industrial oil applications and also applied in removal of toxic elements from polluted water bodies. Substances capable of resisting corrosion are mostly soluble in base oil [18][27]. With high potential in functional groups of physical binding on the surface of elements by creating an active passive layer of defense [6]. For good performance in protecting engine components against degradation effect by oxidation/corrosion on base oil, the layer has to be closely packed to resist water and oxygen penetration [28]. The actualization of this target comes as a result of strong and dipolar groups and oil dissolve tail known as hydrophobicity tendency with unbranched and long alkyl chain [6][29]. Any material (*Eichhornia crassipes*) that contain substances of surface-active molecules with high potential in amphiphilic, chitin and chitosan compounds is known as surfactants [30][31]. With Water hyacinth properties (hydrophobic tail and little hydrophilic tail), contain a unique structure as a surfactant, were the hydrocarbon tail extended into oil phase without losing its properties (insoluble) in water, hence provides good transition between water and oil phase [31]. A successful report on the use of cotton and silica nanoparticles for sorbent application discovered of same behavior with *Eichhornia crassipes*. [20]. The important constituents in *Eichhornia crassipes* that proves it suitable for the application are illustrated in figure 1 below.

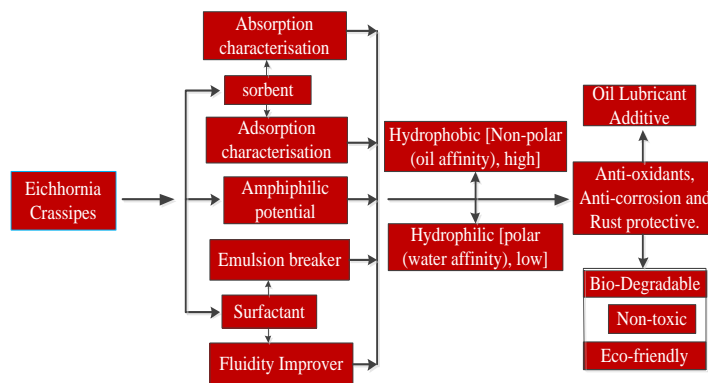


Figure 1. Eichhornia crassipes potentials for anti-oxidants application in oil samples

Eichhornia crassipes with good properties in super-hydrophobic and superoleophilic potentials was carried out with additional support of silica nanoparticles for pure homogeneous mixture. With the optimum mechanical and physiochemical properties of water hyacinth indicates it as one of the best bio-sorbent material in oil treatment processes and also anti-oxidant in performance [28]. All these properties are of paramount essentialities of *Eichhornia crassipes* in this study. Lipids also called phospholipids as found in *Eichhornia crassipes*, are major components of the plasma membrane of water hyacinth and similar to triglycerides with slightly in structure and function [32]. The phospholipids are more in formation of lipid layers, that help in keeping the cell membrane structure [33], as described in figure 2 and 3 below. They are more rigid chemical structure than triglycerides in terms of oxidation stability. In the area of triglycerides, have glycerol and three fatty acids, that makes them fats. Function in maintaining the structure as phospholipids does. Also in resisting contaminants in the structure.

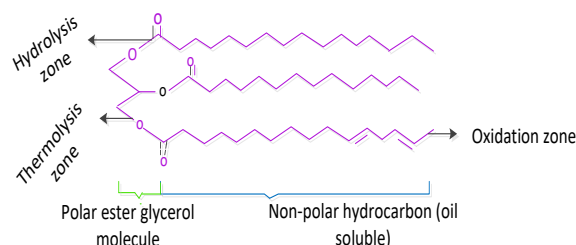


Figure 2: Triglyceride structure of lipid as found in water hyacinth indicating components in chemical reaction [12], [34].

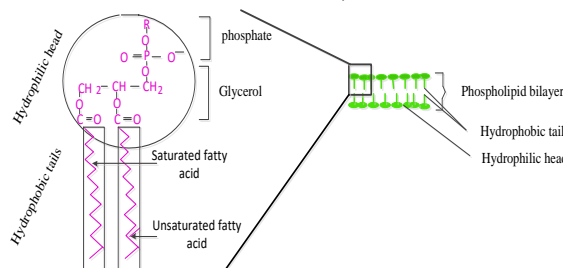


Figure 3: Phospholipid structure of hydrophobic and hydrophilic [33].

A phospholipid is classified as amphipathic molecule of both hydrophobic and hydrophilic parts of different percentages. The tail is made up of non-polar hydrophobic (oil affinity) constituents of fatty acid chains that repels water molecules, while the head is off polar hydrophilic (water affinity) constituents of phosphate-containing group. The membrane of phospholipids is arranged in a structural form called bilayer [32]. In the structure, the hydrophilic phosphate heads attached to the polar materials, whereas the hydrophobic lipids found soluble in the non-polar lubricant as illustrated in figure 3. This arrangement makes it possible for the anti-oxidation performance of prepared water hyacinth in oil sample [33]. If little of phospholipids is placed in an oxidative agent (water and contaminants), it spontaneously forms micelle of sphere-shaped structure. Usually discovered with hydrophobic non-polar faced inside based on the Van der Waals forces of attraction in the oil molecules and hydrophilic polar phosphate heads, attracted outside by the polar materials [35].

III. OXIDATION PHASES OF OIL LUBRICANT IN SERVICE

Lubricant, which consist of hydrocarbon base oil and additives, is subjected to various catalysts with conditions that permits initiation of oxidation to propagate. With these catalysts against base oil and additives, oxidation process sets in and certainly witness degradation. At the initiation phase, hydrocarbon molecules react with developed catalysts, forming some free radical and the reaction continue until perhaps averted by anti-oxidants or lead to complete lubricant degradation as show in figure 4.

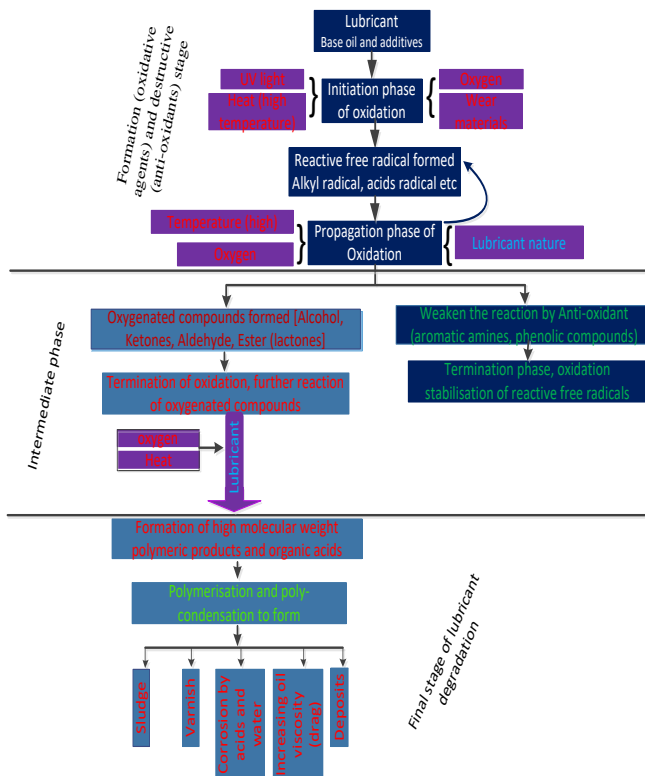


Figure 4. Illustration of oxidation phases in oil lubricant to the final degradation [36].

ree radicals been unwanted constituents in the system and promote oxidation. Highly reactive molecular fragments with one or more unpaired electrons, more prone to reaction with

hydrocarbons and other molecules (hydro-peroxide, alkylperoxy, alkylloxy, hydroxyl etc). propagation continue with these free radicals and further generate oxygenated compounds. Oxidation is a chemical reaction [36], naturally develop between oil sample and oxygen from the surrounding and found to be primary oil degradation mechanism as shown in figure 5.

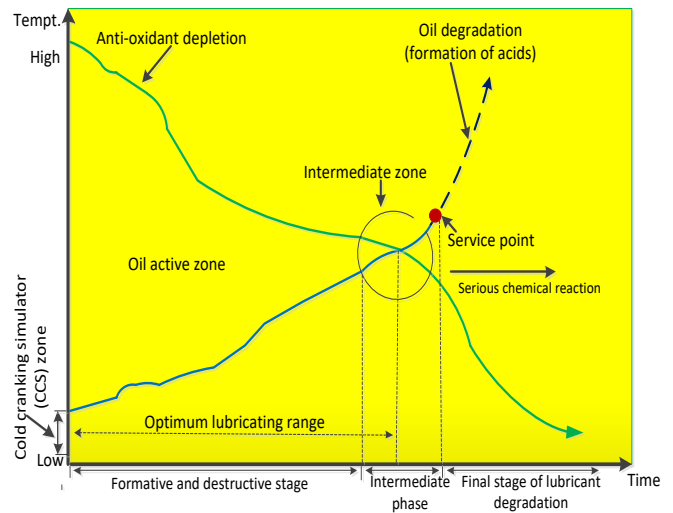


Figure 5. Effect of antioxidant depletion on oil lubricant life.

The process continues as temperatures increase, acids levels increase, active performance of additive decrease (anti-oxidants) [36], and accumulation of fine metal catalysts in the lubricating fluid (oil) is observed. There is an internal promotion of corrosion, pitting, wear, and rust impacts on the metal material surfaces as a result of inability of the lubricant and additives to perform its function.

IV. OXIDATION/CORROSION MECHANISMS IN HYDROCARBON MOLECULES (OIL SAMPLES)

(A). MECHANISM BY ELECTRON TRANSFER

Protection of oil sample from attack of oxidation agents is done using anti-oxidants materials. Since oxygen is in abundant and by nature undergoes some reactions with many inorganic elements or compounds (metals, alkaline metal, alkaline earth metal and others) [37]. During cathodic transfer reaction, electron uptake from oxygen reactive metal surfaces as in figure 6, leading to the formation of activated oxygen specie. The reaction products keep attacking hydrocarbon molecules by abstraction of hydrogen, producing peroxides and carbon radicals. The formed radical of carbon reacts to stabilize through abstraction of hydrogen leaving an alkene as new product.

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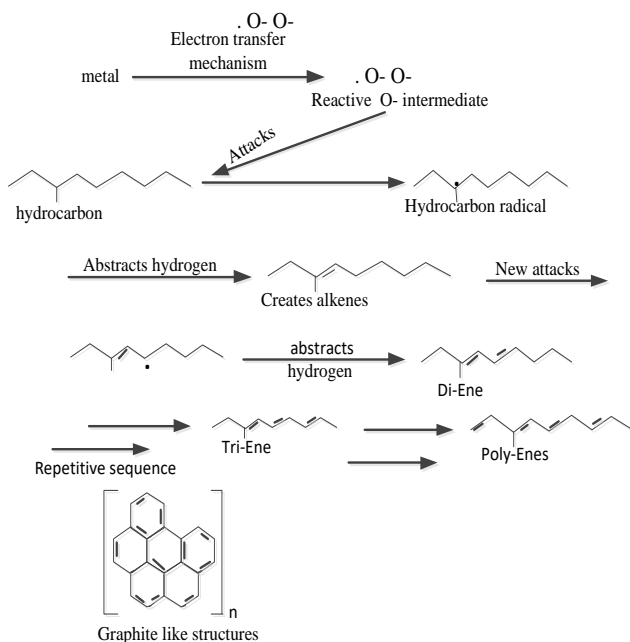


Figure 6. Oxidation mechanisms in hydrocarbon molecules by cathodic reaction [38].

The radical stabilization, with the formulation of alkene products which continue the oxidation process through removal stages of hydrogen. The further yield from that were di-tri, poly-alkenes and benzene rings as illustrated in the figure 3. At this stage of development and reaction in the oil lubricants, the quality of performance together with the tribo-characteristics has been degraded beyond the required.

(B). MECHANISM BY ACTIVATED OXYGEN

Another phenomena of oxidation apart from hydrogen elimination, is also by attacking carbon radicals by oxygen and other oxidants agents. This chemical reaction processes, produces acidic products that is the weakest constituents in oil mixture, illustrated in figure 7.

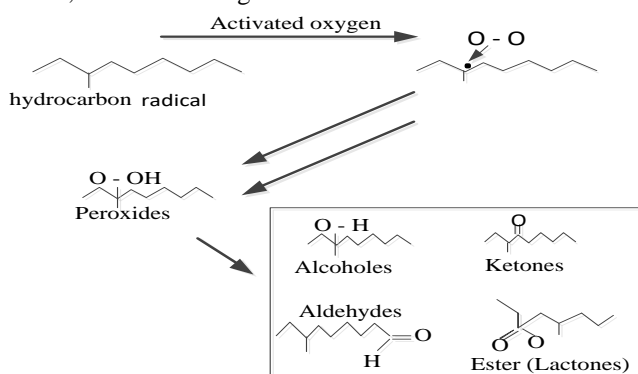


Figure 7. Base oil hydrogen elimination mechanism by activated oxygen [36].

Further reaction of oxygen with assisting oxygenated compounds results in formation of ester (lactones), carboxylic acid and water [36]. At severe temperature, the reaction increases with large of carboxylic acid and others. This persist together with great abstraction of hydrogen from the hydrocarbon molecules. The least formed products from the reaction include alcohols, aldehydes, carboxylic acids, ketones, and esters (lactones) which are compounds of carbonyl group. Formation of insoluble products, organic acids and water, which corrosively attack base oil. Lubricant

viscosity increased (drag) as a result of condensation of ketones and aldehyde in the system [36]. The described effects on the final product of system oxidation from the poly-condensation and polymerisation of the oxygenated compounds. The molecular compounds weight increase turns to form varnish, sludge and deposits.

(C). CATALYTIC MECHANISMS

The group of catalyst for the oxidation of organic compounds are carboxylates of metals shown in figure 8. For good solubility in the organic solvent (oil), these catalysts are highly lipophilic [35].

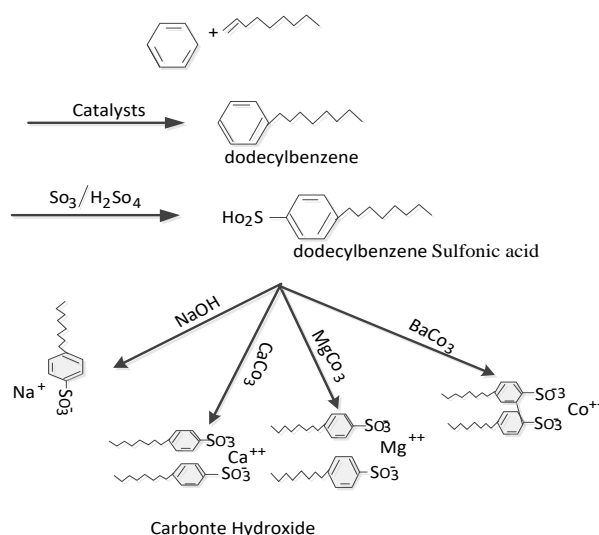


Figure 8. Base oil degradation by catalytic mechanisms[36].

Consequently, they also initiate radical chain reactions (auto-oxidation), forms organic radicals that further combine with oxygen to yield hydroxide intermediates in the process. All these occurrences are strongly supported by the bound energies that exist in the system.

V. ANTI-OXIDANTS CLASSIFICATIONS OF EICHHORNIA CRASSIPES

Antioxidants of natural form are the compounds that are present in mineral oil originally. They could be sulphur and nitrogen heterocyclics and polycycloaromatics or found in bio-oil as in triglycerides known as lutein, lycopene, zeaxanthin, astaxanthin etc [30]. However, the lack of these compounds during processing stages, makes it necessary to compensate and activate the lubricant with appropriate groups of additives. Generally, the available three types of antioxidants in eichhornia crassipes, include; radical scavengers (primary antioxidants), peroxide decomposers (secondary antioxidants) and metal passivators/deactivators [39]. Radical scavengers as found in phenolic, aromatic amines and also in sulfuret and phosphorus compounds which due stop oxidation chain propagation by blocking free radicals, generated in the initiation stage of the reaction. This scavenger's phenomena occur via donation of hydrogen atoms that react with alkyl radicals, with formation of quinones [32], [39].

Peroxide decomposers. Products of *Eichhornia crassipes* are organic in nature, contain little of organic sulphur (dialkylsulfides) and organic-phosphorus (triaryl phosphites) compounds with good potential of hydrogen-peroxides to non-radical derivatives like alcohols [40]. Metal deactivators of N-salicylide ethylamine and benzotriazole, works as surface film-forming compounds of chelating agent (stable complex forming agents) with potential of reducing catalytic effect of metal ions on oxidation. *Eichhornia crassipes* is characterized by high potential of phytoremediation with chelating agent capable of pulling metal ions in their structure in form of stable complexes to repel the catalytic oxidation reaction of the metal ions [30], [40]. The mechanisms of film forming agents, covers the metal surfaces thereby prevents the particles in contacting with the oil phase.

VI. THE CHEMISTRY OPERATION OF ANTI-OXIDANTS IN OIL SAMPLES

The mechanism involves the action of active antioxidants against oxidation agents. Two main principle mechanisms were proposed for antioxidants in service. It started with chain-breaking mechanism which is the first stage. This is done by electrons donate by the primary antioxidants to the free radicals (lipid) [38], present in the lubricant (oil sample). Second stage comes with mechanism of removal of reactive oxygen species (ROS) and reactive nitrogen species (RNS) as the initiator by preventing the continuation of the reaction by chain initiator catalyst as in figure 9.

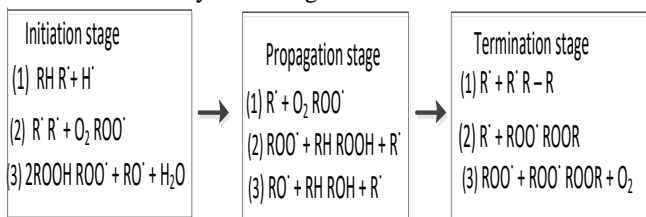
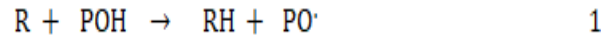


Figure 9. Sequence of antioxidant reaction in oil lubricant [41].

Antioxidants + O₂ oxidized antioxidants, in free radical chain reaction, facts in contact with oxygen to form unsaturated fatty acids which give rise to free radicals thus affecting the hydrogen element in the lubricant. The antioxidants added to it, neutralizes the free radicals by donating one of their own electrons ending the reactions [40]. Termination through breaking the reaction and render the propagation inactive. Chain breaking anti-oxidants with high hydrophobicity, surfactant and sorbent. Such potential as well as aromatic amines or phenolic, react with the free radicals (oxidation agent) to form inert or weak by-products and stable radicals.

VII. THE SCAVENGER OPERATION OF LIPID COMPOUNDS OF EICHHORNIA CRASSIPES IN OIL LUBRICANT

Lipids (phenolics) as free radical scavengers and metal chelator or chitins [41]. Phenolic compounds (POH) of lipids acts as free radical acceptors and oxidation chain breakers. They interfere with oxidation process and other molecules by rapid donation of a hydrogen atom to radicals (R) as in equation 1.



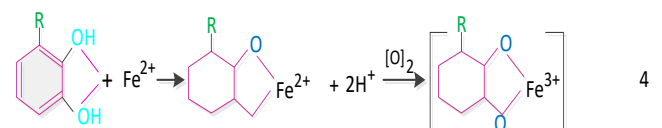
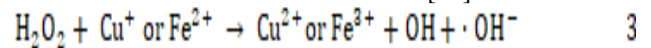
Phenoxy radical (PO·) formed are relatively stable due to its resonance tendency, thus making it so difficult for a new oxidation chain reaction to develop or initiate. Also function as terminators of propagation sequence of reacting with other radicals, illustrated in equation 2.



Lipids compounds of water hyacinth possess potential chemistry structure for free radical scavenging function, owing to the following.

- Phenolic hydroxyl group contains free electron radical and has good tendency of donating hydrogen atom [41]
- Delocalize an unpaired electron through projected conjugated aromatic system.

In the area of metallic ions, phenolic compounds with gallate and catecholate groups can inhibit metal-induced oxygen radical formation either by coordination with Fe²⁺ and enhancing autoxidation of Fe²⁺ as shown in equation 4 below, or serious development of inactive complex with Cu²⁺, Fe²⁺, or Cu⁺ with slow and weaker interaction [35]



In practice, these two active antioxidants in equation 4 above, yield reduction of the steady state action and concentrations of free radicals and oxidant species. As a result, the target of oxidation molecules on antioxidants such as lipids (phenolic acid), ascorbate and flavonoids is diminished [32]. Based on these potential capacities, antioxidant activities of natural phenolics as can be formulated from water hyacinth should be successfully utilized in oil lubricants.

VIII. CONCLUSION

The function and properties of oil lubricant in our industrial machines get diminished due to subjected activities. This unwanted situation developed, mostly based on lubricant inadequate oxidative stability. Modifications as to improve the oxidative property of oil samples with bio-materials are seriously yielding positive results. The achievement is based on the high hydrophobicity and the molecular structure of *Eichhornia crassipes*. The use of bio-antioxidants, well established as relatively effective and cheap of obtaining oxidative stability improvements. The good percentage of monounsaturated compounds with little of polyunsaturated constituents provides suitable oxidation stability and desired fluidity in the system. The performance of these antioxidants shows high resistance of oxidative agents and effectiveness in low percentage of toxicity and eco-friendly attributes. *Eichhornia crassipes* exhibited good synergies with other additives in the oil sample, resulting in optimum solubility in lubricants, also with great amphipathic molecule for good lubrication. The work was seriously investigated and proves natural organic antioxidant operation with good tribological behavior in service owing to the anti-oxidant potentials in the material used.

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Research interest: Automotive Tribology, Friction Material, Lubrication oil. Focusing on friction and wear control in braking system under normal and contaminant environment. Investigating third body, external particle size and shape effect on the friction, wear and noise of the automotive friction material. Also studying the oil palm as bio-oil lubricant for automotive application.



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PROFESSIONAL MEMBERSHIP
Registered with Board of Engineers Malaysia (BEM)
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Member of Japanese Society of Tribologist (JAST)
Member of The Japanese Society for Technology of Plasticity (JSTP)
Member of Japan Institute of Light Metal (JILM)
Member of My Tribos

AWARDS
Distinction Service Award, Universiti Teknologi Malaysia, 2006
Distinction Service Award, Universiti Teknologi Malaysia, 2009

Best Paper Award (Bronze) in ASEAN Conference on Scientific and Social Science Research (ACSSSR 2011)
Outstanding Paper Awards in The 4th International Meeting on Advances in Thermofluids (IMAT 2011)

PROFESSIONAL

University :
Committeemember of FKM promotion
Committee member for the 4th Asian International Conference of Fluid Machinery (AICFM2009)
Committee member for FKM 2009 annual report
Committee member for UTM Innovation & Creativity Festival
Committee member for Konsortium Perisian Terbuka
Committee member of FKM colloquium
Committee member of UTM promotion group
Committee member for Jom Masuk U
Coordinator for course Mechanic of Fluids (I and II)
Coordinator for fluid mechanics laboratory
Coordinator for part-time master programme of FKM
Faculty supervisor for student practical training
Interviewer for Zamalah Scholarship UTM
Interviewer for Degree ++ program
Moderator for SME1902
Moderator for bengkel kejuruteraan
Evaluator for UTM Research University Grant Scheme
Examiner for viva in FKM, UTM
Invited for speech in Majlis Cetusan Pemikiran, Majlis Professor UTM
Member of the MoU with Kagoshima University, Japan.
Leader of the MoU with Orec Ind Sdn Bhd
Chief Editor for Special Edition on Latest Trend in Fluid Mechanics

SERVICES

EXPLORATION

National :
External Examiner for Master (Research) from Universiti Kebangsaan Malaysia
External Examiner for Master (Research) from Universiti Sains Malaysia.
Secretary for the 4th International Meeting on Advances in Thermofluids IMAT 2011
Editorial Board of Journal of Mechanical Engineering and Technology, UTEM.

International

Reviewer for Scientia Iranica
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Reviewer of Engineering Science and Technology (JESTEC)
Reviewer for Journal of MPOB

RESEARCH

Research theme:
Conducting research in bio-lubricant, tribology in metal forming, micro-pitting, palm oil as lubricant, fluid flows.