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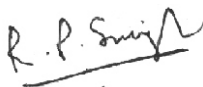# CONTENTS

From Editors Desk

Hello Friends,

In 2018, the world's largest lubricant demanding country emerged out to be China with the market amounting to 7.2 million tons, followed by United States of America with 6.1 million tons. India is the third largest country with the demand of 1.65 million tons. It is forecasted that by the end of 2024, the market value of lubricants in Asia pacific will amount to more than 73 billion US $ making it the largest global lubricant market. The global market is expected to have a value of 188 billion US $.

The increase in power industry is expected to drive the bio-lubricants market in the Asia-Pacific region. The expansion of the automotive sector, particularly in emerging regions such as India, China, South Africa & Brazil are also expected to drive the consumption of sustainable products that contribute to higher fuel efficiency & lower carbon emissions from vehicles.

Plant-based oils have displayed great potential as a substitute for conventional mineral oils since they are structurally similar to the long chained hydrocarbons found in mineral oils. These oils are thus increasingly being utilized for bio-lubricant production owing to their advantageous characteristics such as renewability, non-toxicity, economic & environmental friendliness among others.

Increasing R&D efforts to explore opportunities for bio-lubricant formulation via animal oils & fats is likely to boost segment growth over the time ahead. The market for Bio-Lubricants is anticipated to register a CAGR of over 3% during the period 2020 - 25. Recent researches are focussed on exploring new varieties of vegetable oils like dhaincha oil, bhallataka oil, waste cooking oil etc. New experiments are also being conducted by the researchers, which are focused on optimizing methods for synthesis of bio-lubricants. The methods include chemical modifications via epoxidation, structural modification, and transesterification.

(R.P. SINGH)

BioLubricants and NanoLubricant Additives: A Review

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ABSTRACT

Lubricant industries are focusing on biodegradable materials like modified vegetable oils for the production of lubricants and avoiding the conventional petroleum based lubricants. This is because of their adverse environmental effects as they contain various heavy metals and their salts like Sb_2O_3, Sb_2S_3, As_2S_2, As_2S_4, $AsCl_3$, $PbHAsSO_4$, $PbCO_3$, $HgCl_2$, Hg_2Cl_2, $Hg(NO_3)$ etc. But there is a drawback of vegetable oil based lubricants that they have a higher rate of oxidation and lower viscosity index. Thus we need to conflate some external additives to abstain this trouble. A number of natural and synthetic lubricant additives are being used since longer times to improve the performance of lubricants but natural additives have very limited properties. There are also some petroleum based additives but again they have lesser biodegradability and higher toxicity.

Nano-Technology based lubricant additives are not only eco-friendly but also used in traces unlike the conventional petroleum based lubricant additives. They are helpful in improving the thermal as well as oxidative stability, viscosity index, dispersion properties, better anti-wear characteristics, high biodegradability and various other physicochemical properties.

This review paper encompasses various methods of production of biolubricants, importance of lubricant additives, their methods of synthesis, characterization, properties and advantages of nano lubricant additives over conventional petroleum based additives. Various methods of production of nano-lubricant additives, their properties and their effect on the performance on lubricity and their comparison with conventional petroleum based lubricants has also been discussed in this paper.

1. Introduction:

Lubricants are being used since the invention of wheel. The main function of lubricant is to reduce the frictional force by decreasing the friction coefficient and since that age, lubrication became the basic need for every moving mechanical machine (Madius and Smet, 2009, Honary, 2011).

In any mechanical equipment, the moving part causes a friction force because of the surface irregularities of two superficial contacting surfaces (Zhu et.al, 2007, Rothbart, 2006). Every working surface is rough and this roughness causes thousands of microscopic barriers which generates a reverse force against the movement of that surface. This reverse force is known as friction force (Singer and Pollock, 1992). There are basically two losses induced by friction force that is the loss of energy and the depreciation of material or wear loss which can lead up to the mechanical failure of the engine, gear, bearings or any other moving part of the machine (Bartz, 1978, Demydov et.al, 2010).

The tribological study of energy concludes that 33% of energy from fuel is wasted by friction losses of a moving machine (Holmberg et.al, 2012). The calculation of energy consumption of vehicles reveals that if we consider just heavy duty vehicles like buses and trucks, about 18000 million liter fuel were wasted by friction losses occurred in year 2012 globally (Fox, 2005, Mohamed and Filippone, 2010) which is a shocking figure.

The losses generated by friction can't be overcome but can be reduced up to an extent by the proper lubrication of the machineries. As a result of this, the enhancement of lubricating oil also becomes a big concern (Choi et.al, 2009).

Nowadays, lubricants are produced in a large scale by various methods but mostly they are being produced by petroleum based feed stocks. According to a key note paper, presented by head of global strategic marketing and chief sustainability officer at 16th ICIS world base oil & lubricants market in London, the global lube market volume was at around 31.9 million tons in the year 2009 and increased with 10% in the next year (15, reference not found) that became 36.1 million tons in year 2017. It is estimated that the demand of lubricant

will grow continuously by up to 2-3% per year.

The base material of almost every lubricant is petrochemicals which are obtained by crude petroleum (Rudnick, 2009, Otero et.al, 2014). Although petroleum based lubricants have many useful characteristics yet these are non renewable and toxic to the environment (Wu et.al, 2007).

Some machines like agriculture equipment's, food industries and water pumps have direct contact with food and human lifestyle need a safe and non toxic lubrication. Petroleum based lubricants can cause dangerous contamination if used directly in these fields. Improper disposal of petroleum based lubricants can cause serious contamination in water and can vitally affect the aquatic ecosystem (Aji et.al,2015, Gurram et.al, 2015, Silva, 2011). Also petroleum has limited source which is reducing day by day because of this the price of petroleum based lubricants is also increasing exponentially (Mang and Dresel, 2007).

Major portion of petroleum lubricants end up polluting the environment. The solution of this problem is hidden behind the eco-friendly biolubricants. Biolubricants have zero toxicity to the environment because of their excellent self-degradable properties and the sources of biodegradable lubricants are themselves biodegradable in nature as they are derived by vegetable oils which are produced through renewable sources such as plants, seeds and fruits. That's why lubricant industries are replacing the petrochemical based feedstocks with vegetable oils as base material for synthesis of biolubricants.

Biolubricants can be manufactured by both vegetable oils and animal oils i.e. generally low cost non edible oils. Some of the vegetable oils which are being used for biolubricant production are karanja oil, neem oil (Saroj and Padhi, 2011), palm oil (Ong et.al, 2011), waste cooking oil, rapeseed oil, castor oil (Shahabuddin et.al, 2013), linseed oil, mahua oil (Ong et.al, 2011) and many more.

The main component of vegetable oils used for making biolubricants is triglyceride. The triglyceride is chemically modified for synthesizing the biolubricants. There are various methods of chemical modification of triglyceride like transesterification, epoxidation, synthesis of estolides, synthesis of polyols etc (Kania et.al,

2015). These modifications enhance the physicochemical characteristics of the vegetable oil and make it suitable for lubrication.

Vegetable oils based lubricants have various advantages like high biodegradability, renewability, lubricity, higher flash points, less toxicity and their good anti-wear characteristics still like the two faces of a coin, there are also some disadvantages of bio lubricants which make it unsuitable for using at a large scale i.e. their poor thermal and oxidative stability, higher pour points, lower viscosity index, etc. These drawbacks are also unavoidable as they can broadly impact the lubricant's performance.

To reduce these undesirable properties we need to add some external materials which can modify the lubricant without affecting its positive qualities. These external materials are called lubricant additives. There are hundreds of natural as well as synthetic additives which are being used to modify lubricants performance since centuries. In 1930s natural waxes were used to increase thermal stability and oxidative stability. Some polar solvents like kerosene (Nagendramma and Kaul, 2012) were also used to mix in the lubricant for reducing viscosity but these natural additives had limited advantages (Panchal et.al, 2013).

Nowadays, some polymeric waxes, inorganic compounds and surfactants are being used as multipurpose synthetic lubricant additives. Poly methyl metha acrylate (PMMA) is the most common polymeric lubricant additive which is being used on a large scale by almost every lubricant manufacturer.

Although these additives are somehow fulfilling our desires yet with the technological improvement, lubricant additives have also been modified more and more. The introduction of nano technology has made an evolutional change in the area of lubricant additives.

Nano lubricant additives are fine inorganic elements or compounds, stabilized by surfactants or stabilizers. The main advantage of using nano lubricant additives is its suitable size to enter the contact acuteness, excellent surface reaction and thermal stability (Joly-Puttuz et.al, 2004).

Recent studies in the area of lubricant additives have proved that the addition of surface modified nano particles to the lubricant such as metal sulfides

(Chen et.al, 1998), metal oxides (Battez et.al, 2008), pure metals (liu et.al, 2004), carbonates (Rapoport et.al, 1999), borates (Hu and Dong, 1998), nano Carbon materials (Huang et.al, 2006), organic materials (Rico et.al, 2007), and rare earth metal compounds (Zhang et.al, 2001) has superb effectiveness to the various properties of lubricants (Wu et.al, 2008).

Overall this review paper focuses on various methods of synthesis of biolubricants, their advantages and disadvantages, types of lubricant additives for improving various properties of lubricants accordingly, implementation of nano technology in the area of lubricant additives. Various methods of production of nano lubricant additives, their advantages and disadvantages along with their physicochemical effect on the lubricity of base lubricants are also discussed in the paper.

Table-1: List of chemical reactions for the synthesis of biolubricants along with the catalyst used:

Modification	Catalyst
Modification of Carboxyl Groups	
Esterification/ transesterification	Acids/ Bases
Estolides	HClO4
Modification of fatty acid chains	
Selective hydrogenation	Copper catalysts
Dimerisation/ oligomerisation	Aluminosilicates
Diels-Alder cycloaddition	-
Telomerisation	H2O vapor
Co-oligomerisation	RhCl3.3H2O
-Hydroformylation (oxo-synthesis	Rh(Ph3P)3
Friedel- Crafts alkylation	Et3Al2Cl3
-Aminoalkylation	[Rh(COD)CI]2
Friedel- Crafts acylation	EtAlCl2
Ene-reaction	EtAlCl2, SnO4 Mn(OAc)3, Cu
-Radical addition	Mn(OAc)3, Cu
Acyloxylation	Nafion/ SiO2
Cyclopropanation	CH212, Zn(Cu), Et2Zn
Metathesis	Grubbs catalyst
Epoxidation	Peracids, Chemo- enzymatic
-Ozonation	-
Oxidative cleavage	Pb3O4

Source : A review of bio-lubricant production from vegetable oils using esterification transesterification process conference paper in MATEC web of conferences March 2018

2. SYNTHESIS OF BIOLUBRICANTS AND TYPES OF LUBRICANT ADDITIVES

2.1 Methods used for the synthesis of biolubricants

Biolubricants are synthesized by chemical modification of vegetable oil. There are number of chemical reactions which can be used for modification of triglycerides as shown in the table (Arianti and Widayat, 2018).

As we can see, the vegetable oil based lubricants can be made by so many different chemical reactions but among them only esterification/transesterification, epoxidation, conversion into estolides and conversion into organic polymers are the most used methods for the industrial production of lubricants.

2.1.1. Transesterification

Production of fatty acid alkyl esters by reacting fatty acid or oil with alcohol is called transesterification. This fatty acid methyl ester can be used as biofuel or bio lubricant. The reaction can be catalyzed by both homogeneous catalyst and heterogeneous catalysts (Macario et.al, 2010). The most common catalyst used for industrial production of fatty acid methyl esters is sodium methoxide (Karmakar et.al, 2015). Generally short-chain alcohols such as methanol/ethanol are used (for biodiesel

production) as a base. Low quality feedstocks, including non-edible vegetable oils, animal fats, waste cooking oils, and grease, contain a significant amount of free fatty acids (FFA). When FFA is high, the sodium methoxide catalyst cannot be used because of soap formation. Acid catalysts work much slowly than a base catalyst in a transesterification reaction (Canakci and Gerpen, 2001). Moreover, because of the corrosive nature of acid catalysts; expensive acid-resistant reactors must be used. Therefore, in order to convert a low quality feedstock into biodiesel, first the FFA present in the feedstock should be converted into esters with an acid catalyst to obtain a mixture of fatty acid methyl esters and triglycerides. The esters in the second step are transesterified with methanol catalyzed by a base to obtain biodiesel. The reaction has been depicted in figure 1.
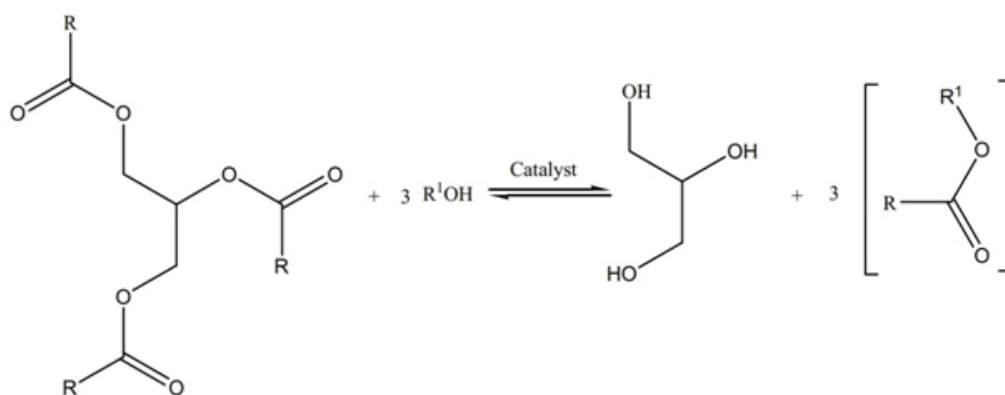
Figure 1: Transesterification reaction of try glyceride for the production of biolubricant (Rico et.al, 2007)

2.1.2. Epoxidation

Epoxides are basically cyclic ethers which contains three elements in the epoxide ring. Epoxidation is one of the most important reactions of unsaturated fatty acids for synthesizing bio lubricants. The double bonds in the vegetable oils are used as reactive sites in various chemical reactions and they can also be functionalized by epoxidation. Therefore the presence of double bond in the fatty acids of triglyceride is mandatory for the epoxidation reaction. The utilization of epoxidized vegetable oils has become more common in the past few years. Epoxidized oil contains epoxide groups or oxirane rings. Epoxidation reaction involves reaction of an alkene with an organic peroxy acid.

Epoxidation reaction generally takes place in two steps:
  (i) Formation of peroxy acid
  (ii) Reaction of peroxy acid with the unsaturated double bond.

The conversion of ethylenic unsaturation into epoxide depends upon various factors like temperature, ratio of ethylenic unsaturation to percarboxylic acids, catalyst & catalyst concentration, rpm and addition time of H_2O_2. Addition of H_2O_2 is done slowly to avoid zones of high peroxide concentration which leads to formation of explosive mixtures (Rico et.al, 2007). The reactions involved in epoxidation are depicted below in figure 2.
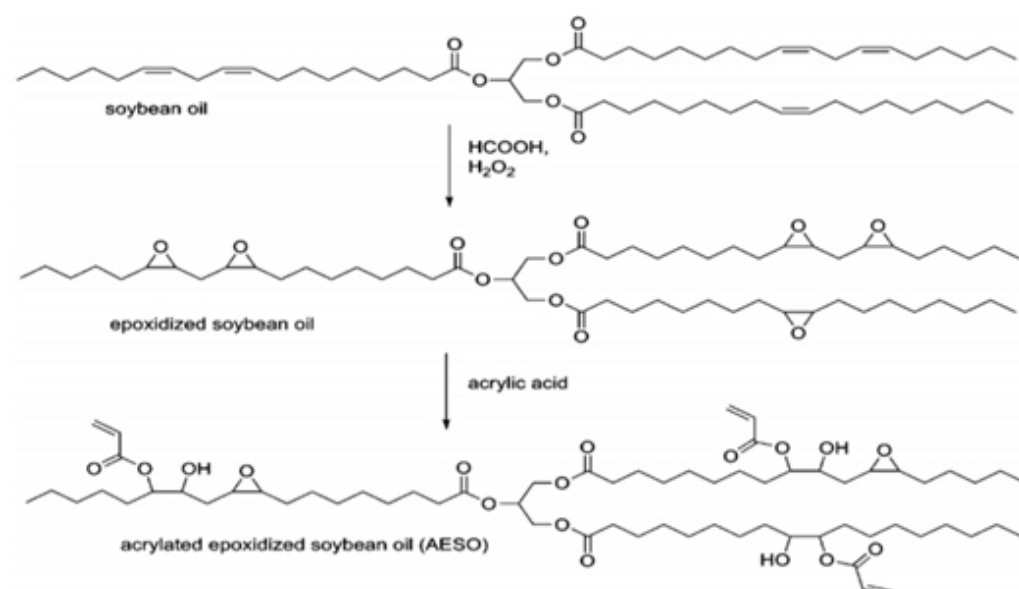
Figure 2: Synthesis of acrylated epoxidized soybean oil (Arca et.al, 2013, Petrovic, 2008)

2.1.3. Synthesis of Estolides

Estolides are also basically esters which are obtained by reaction of both carboxylic group and C=C double bond of a fatty acid molecule. Estolides can be synthesed by both oleic acid and ricinoleic acid by using different acid-catalysts as shown in the figure 3. Arukali Sammaiah et al, 2016 studied the synthesis of estolides from castor oil and methanol using H_2SO_4 as catalyst. These esters have excellent cold temperature properties and oxidative stability. Thus they are used in many industrial applications. Estolides can be used as bio lubricants as well as lubricant additives as pour point depressant. It can be used with different ranges of viscosity depending on their chemical structure, degree of polymerization etc (Rico et.al, 2007).
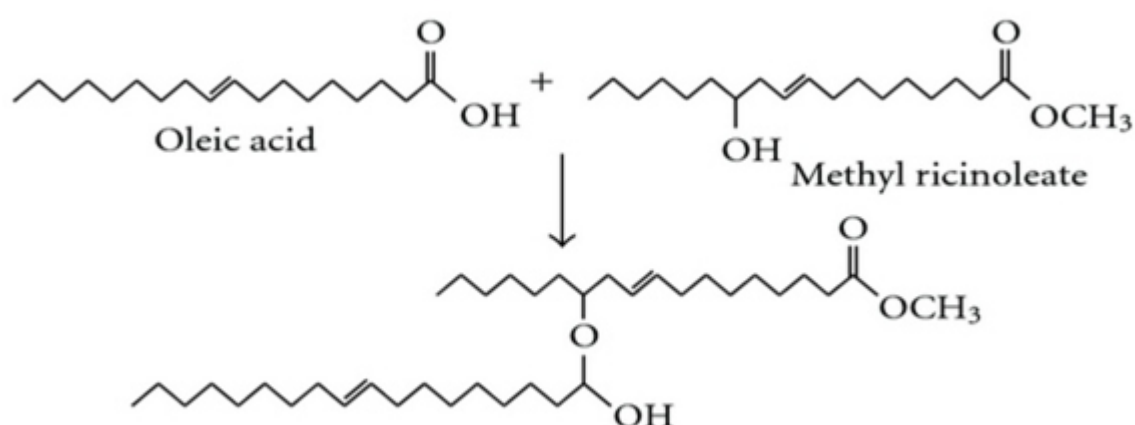
Figure 3: Synthesis of esteloids by oleic acid and methyl ricinoleate

2.1.4. Synthesis of organic copolymers

Biolubricants can also be synthesized by homo polymerization or copolymerization of vegetable oils or fatty esters or their epoxy derivatives with suitable co-monomers. There are various methods of homo polymerization and copolymerization of vegetable oils and their epoxy derivatives for example cationic polymerization, free radical polymerization, ring opening polymerization, and condensation polymerization. Thermally polymerized soybean oil mixed with suitable additives was used as bio-based gear oil. Bio-based polyesters show the extreme pressure additive qualities in mineral oil (Wu et.al, 2007). Polymerization based lubricants show excellent thermal and oxidative stability. Polymerization of vegetable oils and their derivatives in the presence of different organic or inorganic nano-fillers produces polymer nano-composites, which are extensively applied in the automotive industry; especially as an anti-wear coating/additive in lubricants (Can et.al, 2001).

The chemical reactions for the synthesis of polymerized soybean oil are shown below in figure 4.
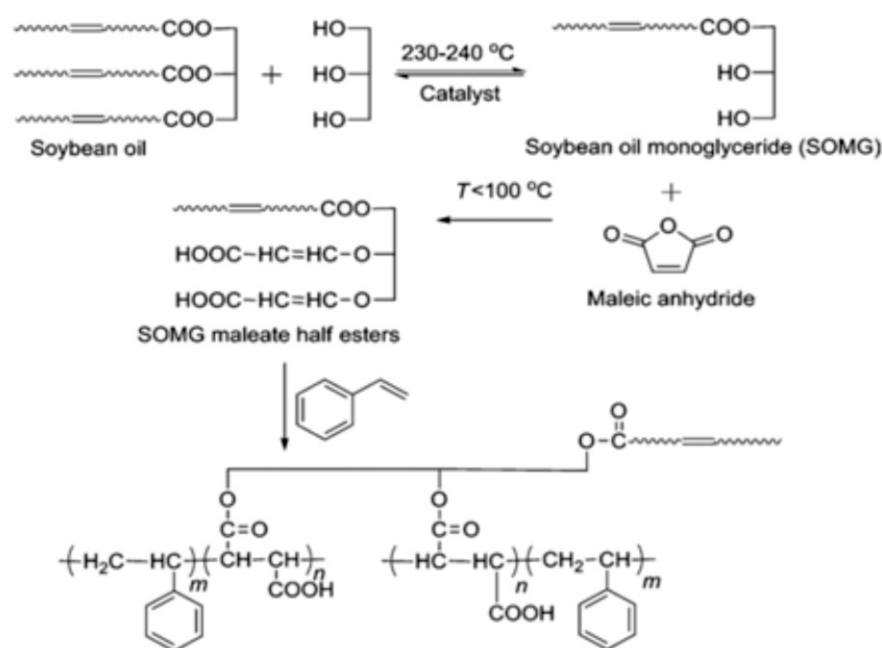
Figure 4: Synthesis and polymerization of soybean oil mono glyceride maleates (Can et.al, 2001)

2.2. LUBRICANT ADDITIVES

Additives for the lubricants may be both organic and inorganic compounds in nature which are suspended in the base lubricant to enhance its performance. They typically range between 0.1 to 30 percent of the lubricant oil volume, depending on the requirements. The basic purpose of a lubricant additive is to;

➢ Improve the properties of lubricants with the addition of antioxidants, anti-foam agents, corrosion inhibitors and demulsifying agents.

➢ Impart new properties to the lubricant with extreme pressure additives, detergents, metal deactivators and tackiness agents.

➢ Reduce the undesirable properties of lubricants with pour-point depressants and viscosity index modifiers.

On the basis of performance of base lubricant and the effect on physicochemical properties, the lubricant additives can be classified as:

2.2.1. Pour Point Depressants

The performance of a lubricant to flow under low-temperature and low-shear conditions is crucial for lubricity. If the equipment runs below pour point, the lubricant leads to its worst condition and becomes solid which causes the equipment failure. Earlier in 19th century, this problem was being

reduced by adding any solvent like kerosene but it affects the viscosity also. There were some other alternatives like addition of microcrystalline paraffin waxes asphaltenic resins etc. Unfortunately these materials were effective but not broadly applicable. Nowadays, the poly alkyl methacrylates are worldwide used pour point depressant they are synthesized by the mono polymerization of vegetable oils with alkyl methaacrylate. The most common example of poly alkyl methacrylates is poly methyl methaacrylate (PMMA).These are nothing but only synthetic waxes which gives the better results than natural waxes (Rapoport et.al 1999).

2.2.2. Viscosity Index Improvers

The most important characteristic of a lubricant is its viscosity. It is the measure of inner friction which works as a resistance to the change of molecular positions in fluid flow when they are under the impact of shear force. In other words, it is the resistance of fluid particles to shear. The viscosity index improvers impact the oil behavior as far as flow characteristics are concerned. The main characteristics of viscosity index improvers are:

> Maintaining the oil in liquid form at lower temperature.
> At higher temperatures they provide higher viscosity to oil which helps in providing a necessary oil film thickness and small oil consumption.

There are basically 3 most known V I Improvers i.e.
  o Poly methacrylates (PMA),
  o olefin copolymers (OCP),
  o Hydrogenated styrene-diene copolymers.

2.2.3. Antioxidants

Oxidation is one of the major problems for biolubricants which occurs because of the open exposure of lubricant to air and catalyzed by metal ions.

Antioxidants are defined as the chemicals which can reduce the rate of oxidation upto a desirable extent. According to the mechanism of action, antioxidants are classified into 3 parts;
  o Primary antioxidants (radical scavengers)
  o Secondary antioxidants (Peroxide decomposers)

  o Metal deactivators (complex-forming or chelating agents) (Majid et.al, 2018).

The most used antioxidants for lubricants are: tocopherols, propyl gallate (PG), ascorbyl palmitate (AP), and some synthetic antioxidants butylated hydroxy anisole (BHA), butylated hydroxy toluene (BHT), mono tert-butyl hydroquinone (TBHQ), or 4,40-methylenebis(2,6-di-tert-butylphenol) (MBP)) which have been used for improving their resistivity towards oxidative agents.

In recent researches, several cellulose fatty esters have also been developed as the lubricant additive, and are modified to cellulose ferulate, cellulose lipoate and α- tocopherulate mainly for antioxidant applications (Majid et.al, 2018).

2.2.4. Anti-Foaming agents

Foams are thermodynamically unstable dispersions of a gas in a liquid. Formation of foam causes more interaction of air with lubricant which increases the rate of oxidation. Besides this, the formation of foam causes the excessive wear in machine parts, less lubrication, poor heat removal, and overall high energy losses. Thus antifoaming agents become the critical part of the lubricants. Silicones are considered as the best antifoaming agents but they have limited use in lubrication. Some other polymeric hydrocarbons like polyacrylates, polypropylene glycols (PPGs) and EO/PO copolymers are also effective foam control agents because of their low foam characteristics and inverse water solubility. These products are available in liquid form, with different molecular weights and viscosities to meet diverse needs (Binks et.al, 2010)..

2.2.5. Metal Deactivators

Metal deactivators are chelating agents which inhibits or reduces the metal ions produced by oxidation or undesired acidic or basic action on the metal surface.

The metal ions catalyzes the rate of oxidation and causes the formation of metallic bases which reduces the performance of lubricant and its self life. The most used metal deactivators are; Salpn ligand (N,N′-bis(salicylidene)-1,2-propanediamine) and EDTA (Ethylene diamine tetra acetic acid) (Yu et.al, 2010).

2.2.6. Anti-Wear Agents

Anti wear agents inhibits the performance of a lubricant by preventing the metal to metal contact of any equipment. They form a thin layer between two metal surfaces by chemical deposition or adsorption. Thus these additives do not only work as an anti wear agent but also reduces the friction upto an ambient pressure. Although we have to use some extremes pressure additives for dealing with high pressure but for low pressures, the anti-wear agents are enough for reduction in friction.

The common Anti wear agents used as lubricant additives are; sulfurized vegetable oils, tritolyl/-phosphate, chlorinated paraffin, alkyl-and aryl di-and tri-sulfides, triphenyl phosphorothionate (Yu et.al, 2010).

2.2.7. Corrosion & Rust Inhibitors

Corrosion inhibitors are the compounds which reduces the corrosion of metals like copper aluminums zinc etc. whereas Rust inhibitors prevent the corrosion of iron by making a protective film or by adsorbing on its surface. These additives are used in traces. The anticorrosion additive concentration equals about 0.1-2% (Ravikovich, 1996). Table 2 shows the various types of corrosion inhibitors along with their uses and examples.

Table 2: Types of corrosion inhibitor their uses and examples (Ravikovich, 1996)

Corrosion inhibitor	Uses	Example
Sulfur-containing corrosion additives	To prevent corrosion of lead- copper bearings, sulfuratedterpines	Di-(3,3,5- trimethylhexyl), sebacateDi(2-ethylhexyl)- sebaeate
Nitrogen-containing corrosion additives	To prevent corrosion of light metals	Benzotriazole, benzimidazole, imidazole, 1,2,3- triazole, 2-methylbenzimidazole, 3,5-dimethyltriazole, or 3,5-dimethylbenzotriazole
Sulfur, Nitrogen and Phosphorus - containing corrosion additives	For esters and Mineral Oils	Tri(alkylamido)-thiophosphates
Boron- containing corrosion additives	To prevent corrosion of copper- lead alloys	P-xylylenediamine and glycol-boric acids
Other corrosion inhibitors	To prevent corrosion of bearings	Phthalic acids and ternary amines or hydroxylalkyl amines

2.2.8. Detergents

Detergents work in two ways. They neutralize the acid produced on the surface of metal as well as they suspend the impurities by suspending it inside. Thus detergents do not only keep the metal surface clean at high temperature but also prevents the corrosion by neutralizing the acids.

Detergents used as lubricant additives are generally anionic surfactants which provide the reverse alkalinity to the base lubricant. Generally higher molecular Calcium, Magnesium, Barium or Sodium based surfactants are used as detergent additives. These surfactants works as a cleansing agent also by trapping the impurities (dirt, water, fuel, process material, and lube degradation products such as sludge, varnish, oxidation products) by forming the micelle and trapping the impurities inside in a suspended form as shown in figure 5 .
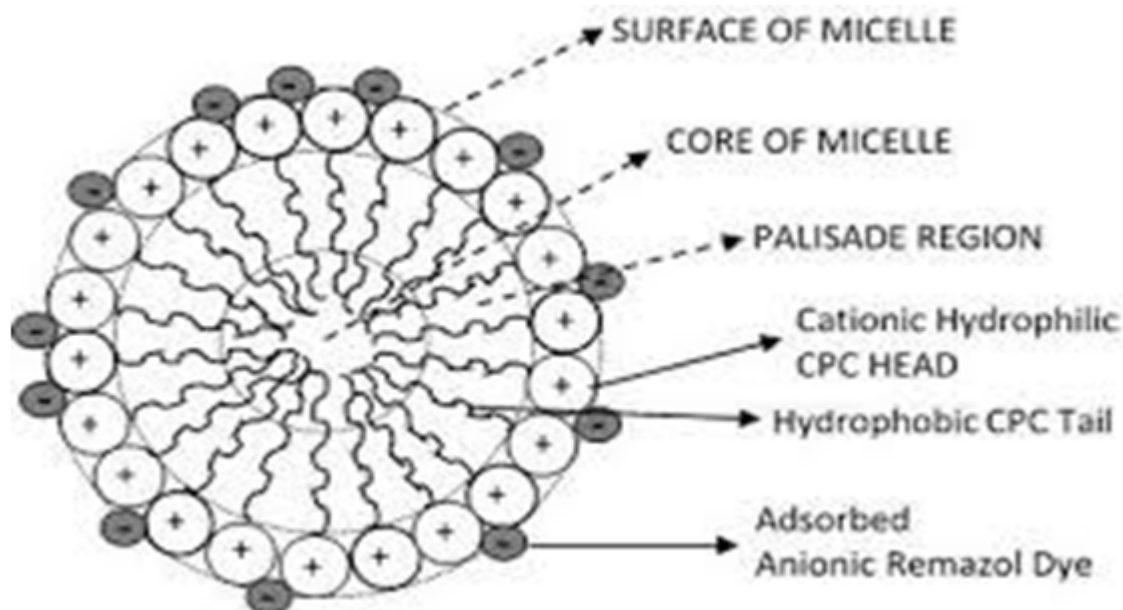
Figure 5: Micelle structure: Structural Biochemistry/Lipids/Micelles technologies.

2.2.9. Dispersants

Dispersants are used to keep the base lubricant free from contaminants. It suspends the impurities and does not allow it to agglomerate. They are used as a mixture of detergents and dispersants. The mixture of detergent with dispersant are more suitable for neutralizing the acidic contaminants and provides better dispersion of impurities.

Dispersants form a protective film on the surface of metal which prevents the contact of metal to air which reduces the rate of oxidation and deposition of sludge and dirt like impurities.

The common dispersants used as lubricant additive are Polymeric alkyl thiophosphonates and alkyl succinimides, organic complexes containing nitrogen compounds.

2.2.10. Friction modifier

Friction modifiers are the oldest additives used for lubricating oils as they fulfill the most desirable requirement of lubricants that is reduction of friction between two metal surfaces.

The long chain fatty acids were the well used friction modification in 1990s. Earlier it was observed that organic surfactants have also more friction reducing capacity than free fatty acids. They work by forming a thin layer between two metal surfaces and prevent the direct metal to contact. The main challenge for a friction modifier is that it must work properly at different physical conditions. They should retain their effectiveness in a range of temperature and pressure. The common friction modifiers used as lubricant additives are; Organic fatty acids and amines, lard oil, high molecular weight organic phosphorus and phosphoric acid esters etc.

3. Nano-Lubricant Additives

There are large numbers of lubricant additives used for fulfilling the different types of requirements. Some specific additives are being used for fulfilling a desired purpose and also there are some multipurpose additives which fulfill more than one requirement at the same time. For example, Silicones are just used for fulfilling anti foaming characteristic; there is no other application of silicones, but on the other hand poly methyl acrylates, act as a viscosity index improvers, friction modifiers, pour point depressants and also enhance thermal stability simultaneously. The recent research in lubricant additives shows that the nano based lubricants have significant impact on the performance of lubricants. These additives have superior performance than conventional polymer based additives. (Hudson et.al, 2006)

L.K. Hudson et al, 2006 studied the preparation of

nano based lubricant additives by overbasing process. The mechanism of overbasing is based on macro emulsification process. The reaction system consist an excess of nano sized inorganic base material, a suitable surfactant, and an appropriate polar solvent like mixture of water and alcohol. The reaction causes the formation of micelle which includes the inorganic base material trapped inside the micelle and the outer layer is formed by some sort of surfactant. This method is also called the Oxide/Hydroxide process when the base material is taken as an inorganic metal hydroxide.

3.1. Structure of nano-Lubricant Additive

The nano based lubricant additive has a micelle like structure in which the fine nano sized inorganic base particles are trapped into a surface active agent like any surfactant or soap. Thus the structure of a nano lubricant additive can be categorized into two parts as shown in figure 6.

1) The outer part of the micelle i.e. any surfactant or soap

2) The inner part of the micelle i.e. any sort of inorganic base (Connor et.al, 1994).
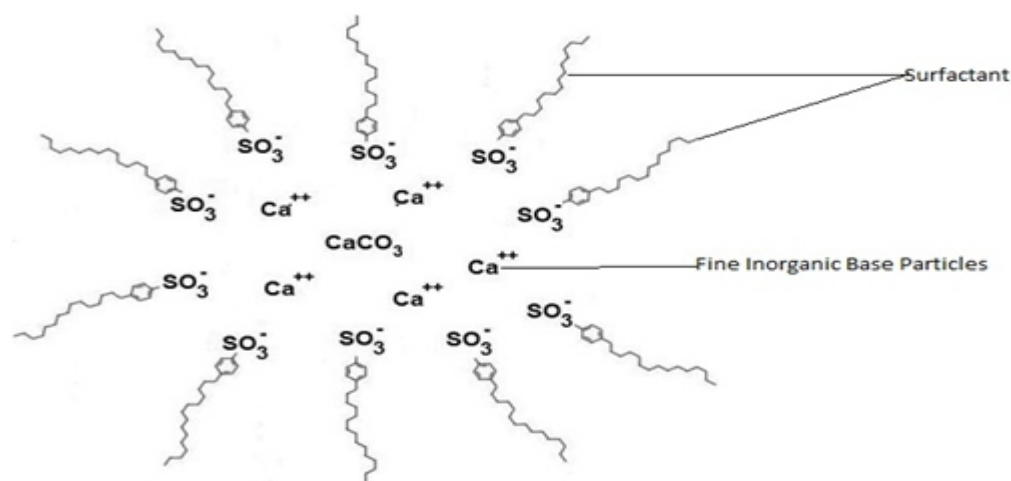
Figure 6: Structure of nano lubricant: Diesel Engine Lubricants, Hannu Jääskeläinen, W. Addy Majewski

3.1.1. Selection of surfactant

The surfactants form the outer layer of the micelle of nano based lubricant additives. Thus it plays the most important part in the efficacy of additive. There are hundreds of surfactants used for nano lubricant additive manufacturing such as salicylates, silicates, sulphonates, carboxylates, phosphinates, alkyl phenates, sulfurized alkyl phenates, sulfurized phosphonates etc according to their performance and requirements. Sometimes the mixture of more than one surfactant is used to form more efficient lubricant additives. The desirable concentration of surfactant mixture can be calculated hydrophile-lipophile balance (HLB). Ruijin Wang et al, 2018 analyzed the respective properties of several surfactants which are tabulated below in table 3(Rujjin et.al, 2018):

Table 3 : Properties of surfactants as stabilizers for Nano Lubricant Additives :

Detergents	Approx. TBN range	Hydrolytic Stability	Oxidation Stability	Thermal Stability	Detergency	Rust inhibition	Antioxidant
Phenates	0-300	Good	Very good	Excellent	Good	Low	Very good
Sulphonates	0-500	Moderate	Poor	Excellent	Good	Good	None
Salicylates	0-300	Good	Very good	Excellent	Good	Low	Very Good
Phosphonates	0-80	Moderate	Good	Moderate	Excellent	Good	Good

3.1.2 Selection of Inorganic base material

The inorganic base material is the second most important part of a nano based lubricant additive as it acquires the inner core of the micelle. It may be any kind of inorganic base or metal of nano size. But according to cost and performance, the most commonly used core materials are calcium, magnesium, sodium, zinc, boron, nickel, carbon and their basic hydroxides, salts and alloys. Sometimes the mixture of more than one material is used as a nano base material (Honary, 2011). Among these, the $Ca(OH)_2$ is one of the most used base material as core which is carbonized with CO_2 at high temperature and pressure before overbasing (Rujjin et.al, 2018).

According to the chemical composition, inorganic base material of a nano lubricant can be categorized as:

3.1.2.1. Metal Nano -Particles as base material

Nano metal particles are high surface active powdered materials. They are being used as catalysts, semiconductors, magnetic and photonic field since long ago. They show the excellent tribological effectiveness and self-repairing properties as well. Because of high surface activity, they shows very less effect on the efficacy of base oil but their performance can be modified by surface modification techniques or overbasing (Padgurskas et.al, 2013). Overbased nano metal based lubricant additives show a tremendous effect. There is a number of metal based nano lubricant additives used as per requirements:

Padgurskas J. et al, 2013 analyzed nano copper based lubricant additives which are commonly used as diesel engine lubricants. It shows the excellent friction wear and self repairing properties. Iron and Tin based nano additives are used in space industries for lubrication and anti wear properties.

3.1.2.2. Metal oxide and hydroxide as base material

Metal oxides and hydroxides are relatively cheaper than pure metals because of the ease of conversion of metal oxides and hydroxides into nano size. The most common metal hydroxide is $Ca(OH)_2$ which is carbonated with CO_2 at high pressure and then overbased with any surfactant. Besides it, some other oxides as TiO_2, ZnO, $ZnAlO_3$ etc has also shown a positive effect on lubricant performance

Wu Y.Y. et al, 2007 analyzed TiO2 and also CuO behaviors as nano lubricant additives. It was shown that the addition of two different nanoparticles to oil decreases its friction (CuO performed shown better results than TiO2 (Wu et.al, 2007).

Silva J. D. et al, 2006 found that ZnO has a very high anti corrosive and anti wear behavior and increases the oxidative stability. $ZnAlO_3$ also has a tremendous dispersive ability and thermal as well as mechanical stability. It is being used in aerospace industries as catalyst, ceramic and anti thermal coatings.

Recent research shows that the mixture of more than one oxide and hydroxides has enormous effect on dispersive properties (Tang et.al, 2006).

3.1.2.3. Boron compound nano particles as base material

The use of Boron compounds as base material is yet a matter of research still a lot of research has been done in the field of Boron compound based lubricant additives. Zaho G. et al, 2014 studied that the nano Calcium borate synthesized by ethanol supercritical fluid drying shows the wonderful load carrying and anti wearing capacity when used with lithium grease. The nano Zinc Borate shows a good anti wear and friction reducing properties with sunflower oil base material. This is also a best alternative of ZDDP for engine oil lubrication (Zhao et.al, 2014)

3.1.2.4. Nano carbon particles as base material

The scope of nano carbon is magical in lubricating industries. There are basically three isotopes of carbon which are generally used as nano materials i.e. Graphite, Fullerene, and Diamond. The friction and friction coefficient can be controlled by Graphite and Fullerene isotopes. Graphite nano particles are used as solid lubricants also in cutting tools (Sheida et.al, 2016).

Nano carbon particles are classified into four parts i.e. zero dimensional nano carbon, one dimensional nano carbon, two dimensional nano carbon and three dimensional nano carbon.

The use of different types of nano carbon is tabulated below in table 4.

Table 4 : Types of nano carbon along with their example and uses

Nano-Carbon	Example	Uses
Zero dimensional	Fullerene	Friction modification, Adsorption
One dimensional	Carbon nanotubes	Wear and Friction Behaviour
Two dimensional	Graphene	Anti wear and Friction modification
Three dimensional	Graphite, Diamond	Ball bearing, solid lubrication

3.2. Method of synthesis of Nano-Lubricant additives through Overbasing

The process of manufacturing is based on the Nano emulsification or ultrafine emulsification where the colloidal solution of nano particles is formed with the help of suitable surfactant or mixture of surfactants (Milton J. Rosen). The methods of nano emulsification can be classified as:

3.2.1. Two step method

This is the most widely used method for preparation of nano emulsions. In this method, the inorganic base material is dried and converted into nano particles in the first step and then this powder is dispersed into a solvent with the help of ultra sonic mixing, magnetic force agitation, high shear mixing and ball milling in step two. This suspension has a very high tendency of coagulation as the nano particles are highly surface active materials. Thus we need to stabilize this suspension with a mixture of surfactant (Wei and Huaqing, 2012). Two-step method is one of the most economic methods to produce nano fluids on industrial scale, because nano powder synthesis techniques have already been scaled up to large scale production.

Due to the difficulty in preparing stable nano fluids by two-step method, several advanced techniques are developed to produce nano fluids, including one-step method.

3.2.2. Single step method

Single step method for production of nano emulsion involves different types of chemical reactions to convert the core material into suspended form. And the suspension is then stabilized by surfactants. This process does not require drying or milling or high shear mixing as the suspension process is done with chemical reactions. And the suspension, formed by this process is a homogenous colloidal solution. The chance of coagulation of emulsion is also less than

two step process. But the main drawback is that this process needs a specific chemical reaction and physical conditions for the formation of a particular colloidal solution. That is why this process can't be applied for industrial scale production. The process is generally used for research purposes (Eastman et.al, 2001)

3.2.3. Other methods

There is some advance research related to nano emulsion formation as; Ethanol Supercritical fluid drying for production of Calcium borate (Zhu et.al, 2007), Phase-transfer method is also used to obtain mono disperse noble metal colloids and kerosene based Fe_3O_4 nano fluids (Yu et. al, 2010), Chemisorption of fluid can also be used for kerosene based Fe_3O_4 nano fluids (Wang and Fan, 2010).

4. ENHANCING THE STABILITY OF NANO EMULSIONS

The stability of emulsion is acquired by add the detergent. The process of stabilization is very simple as we directly add the required amount of surfactant with a medium agitation. The amount of surfactant required can be calculated by HLB method. The surfactant contains a hydrophobic carbon chain and a hydrophilic group which causes the formation of micelle and traps the inorganic base inside. The types of surfactants have been discussed before (Tang et.al, 2006).

5. ADVANTAGES OF NANO LUBRICANT ADDITIVES OVER CONVENTIONAL ADDITIVES

The performance of a nano lubricant additive depends on their base material and the surfactant used for surface modification of that base material. In short we can say that every nano lubricant additive have their own specifications, But the one

thing, which is common in all types nano additives is its smaller particle size and this is the most special thing of it. Lubrication is a surface phenomenon and the smaller particle size makes a lubricant additive more likely to show its performance (Soares et.al, 2007, Tang et.al, 2006, Wu et.al, 2007, Zhao et.al, 2014).

6. CONCLUSION

A huge amount of pollution caused by toxic petroleum based lubricants can be controlled by replacing them with vegetable oil based lubricants. But the limitations of biolubricants over petroleum based lubricants are their thermal stability, oxidative stability and viscosity index. These limitations can be overcome by adding some lubricant additives. There are many additives which are currently used by lubricant manufacturers according to requirements and their performance. However more improvements are required and can be done with the help of nano technology in the area of lubricant additives.

Introduction of nano technology has shown enormous advantages in the field of lubricant additives because of their high reactivity, excellent biodegradability and zero toxicity. Although the technology of manufacturing of nano lubricant is expensive yet it can be adopted as they are used in traces as compared conventional additives.

7. SUGGESTIONS FOR FUTURE ASPECTS OF RESEARCH

Nano lubricant additives have lots of advantages in lubrication applications. However, there is scope of still more improvements to enhance the performance of nano lubricants to make them suitable for being used at industrial scale.

o The process of conversion of normal sized particles into nano particles which is used for the synthesis of nano additives for lubricants is very costly and time consuming process. More research is required to develop cost effective and time efficient process for synthesis of nano particles.

o Stability of nano lubricant additives is very important as the nano materials are highly surface active compounds and they have a tendency of rapid coagulation. Further research for developing surfactants and their mixtures which can be effective in stabilizing the nano lubricant additive is required.

Nano particles of nano additives and surfactant are selective in nature. Every nanoparticles and surfactants of nano additive of lubricant have their own specialties and selectivity. Therefore identification of the specialties and selectivity of nano particles and surfactants for nano additives for lubricants is a potential area for future research.

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Utilization of Bhallaataka (*Semecarpus anacardium* Lf)-Residue Oil in the Development of Biolubricant Basestock

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ABSTRACT

Bhallataka kernel residue oil (BO) was explored for its use as a feedstock for biolubricants. Epoxidized bhallataka kernel oil (EBO) was prepared by peroxyformic acid generated *in situ* by reacting formic acid and hydrogen peroxide in the presence of sulphuric acid as catalyst with oxirane value 3.77. EBO was characterized using IR, ^{1}H NMR, ^{13}C NMR, GC and GC-MS spectral techniques and evaluated for lubricant properties namely kinematic viscosity, viscosity index, copper corrosion, pour and flash point, wear, oxidation and thermal stability using standard ASTM and IP methods. EBO exhibited superior oxidation and thermal stability and enhanced viscosity compared to BO. The lubricating properties of EBO matched well with other epoxide oil properties. Hence, EBO can be projected as a potential source of high temperature lubricant basestock.

KEYWORDS:

Epoxidation, *Semecarpus anacardium, Bhallataka oil,* Lubricants, Oxidation stability

1. INTRODUCTION

Increasing global environmental awareness has encouraged the production of environmentally friendly lubricants. The production and use of non-toxic and biodegradable lubricants has become a major issue, especially when the lubricant involved will come into contact with soil, crops or ground water. Vegetable oils are viable and good alternative resources because of their environment friendly, non-toxic and readily biodegradable nature. The triacylglycerol structure with long fatty acid chains and presence of polar groups in the vegetable oils make them amphiphilic in character, therefore allowing them to be an excellent choice as lubricants and functional fluids (Rudnick 2002). Other advantages include renewability, low evaporative loss due to the high molecular weight of the triglyceride molecule, high viscosity index, good lubricity and high flash point (Fox and Stachowiak 2007). In addition, vegetable oils have high solubilizing power for polar contaminants and additive molecules. However, vegetable oils have poor oxidative and thermal stability, which is due to the high degree of multiple C-C unsaturation in fatty acid chain and the bisallyic protons (Becker and Knorr 1996; Gapinski *et al*., 1994). Chemical modification of vegetable oils can overcome these shortcomings, by reducing or eliminating unsaturation in vegetable oils. These changes can significantly increase the performance of a lubricant material (Hwang and Erhan 2001; 2002; Hwang *et al*., 2003). Epoxidation is one of the most important double bond addition reactions. In case of unsaturated fatty acid esters, it is often performed *in situ* using the per formic acid method. This process is industrially performed on a large scale. The use of epoxidized unsaturated fatty acids as lubricating additives to eliminate corrosion from chlorine containing compounds in metal working fluids is reported in literature (Watanabe *et al*., 1988; Tao *et al*., 1996). The improvement of lubricity properties of vegetable oils upon the introduction of epoxy has also been demonstrated (Adhvaryu and Erhan 2002; Sammaiah *et al*., 2014; Wu *et al*., 2000). Epoxidized vegetable oils and their alkyl esters are commercially useful as plasticizers and polymer stabilizers (Biermann *et al*., 2000). Non-traditional oils like Mahua (Goud *et al*., 2006), cotton seed (Dinda *et al*., 2008), rubber seed (Okieimen *et al*., 2002), karanja(Geethanjali *et al*., 2013; Goud *et al*., 2006) and jatropha(Daniel *et al*., 2011; Goud *et al*., 2007; Goud *et al*., 2010; Meyer *et al*., 2008; Rios *et al*., 2011) were epoxidized using various catalysts. *Semicarpus anacardium* which belongs to anacardiaceae family is a moderate-sized deciduous

tree found in the outer Himalayas and hotter parts of India up to 3500 ft. height. The plant is found in abundance in Assam, Bihar, Bengal and Orissa, Chittagong, central India and western peninsula of East Archipelago, Northern Australia, Malaysia, Myanmar, Singapore, China, and Africa (Kirtikar *et al.*, 1975). The fruit of the tree is a nut which is commonly known as 'marking nut' and in the vernacular as 'Ballataka' or 'Bhilwa'. The pericarp of the nut yields blackberry oil know as bhilawan oil. It is rich in phenols and is used as a base for varnishes. It also has applicability in indigenous system of medicine[2] (Chopra *et al*., 1982; Khare *et al*., 1982). The seed kernel yields reddish brown oil and no detailed chemical investigations had been carried out on the seed oil of *S. anacardium*, while the nut shells had been investigated extensively (Ramadan *et al*., 2010). In the present study the residual kernel oil is exploited for the preparation of its epoxy derivative and evaluated for its potential as a lubricant basestock.

2 EXPERIMENTAL

2.1 Materials

Semecarpus anacardium L.f. nuts were collected from field area very nearer to the village Nandgaon, Kolhapur City, Maharashtra, India. Sulphuric acid, aqueous hydrogen peroxide(30%),sodium sulphate and sodium methoxide were purchased from s.d .Fine chem. Ltd. (Mumbai, India). n-Hexane, methanol and ethyl acetate (LR were purchased from Industrial Solvents and Chemicals Pvt. Ltd., Mumbai, India.
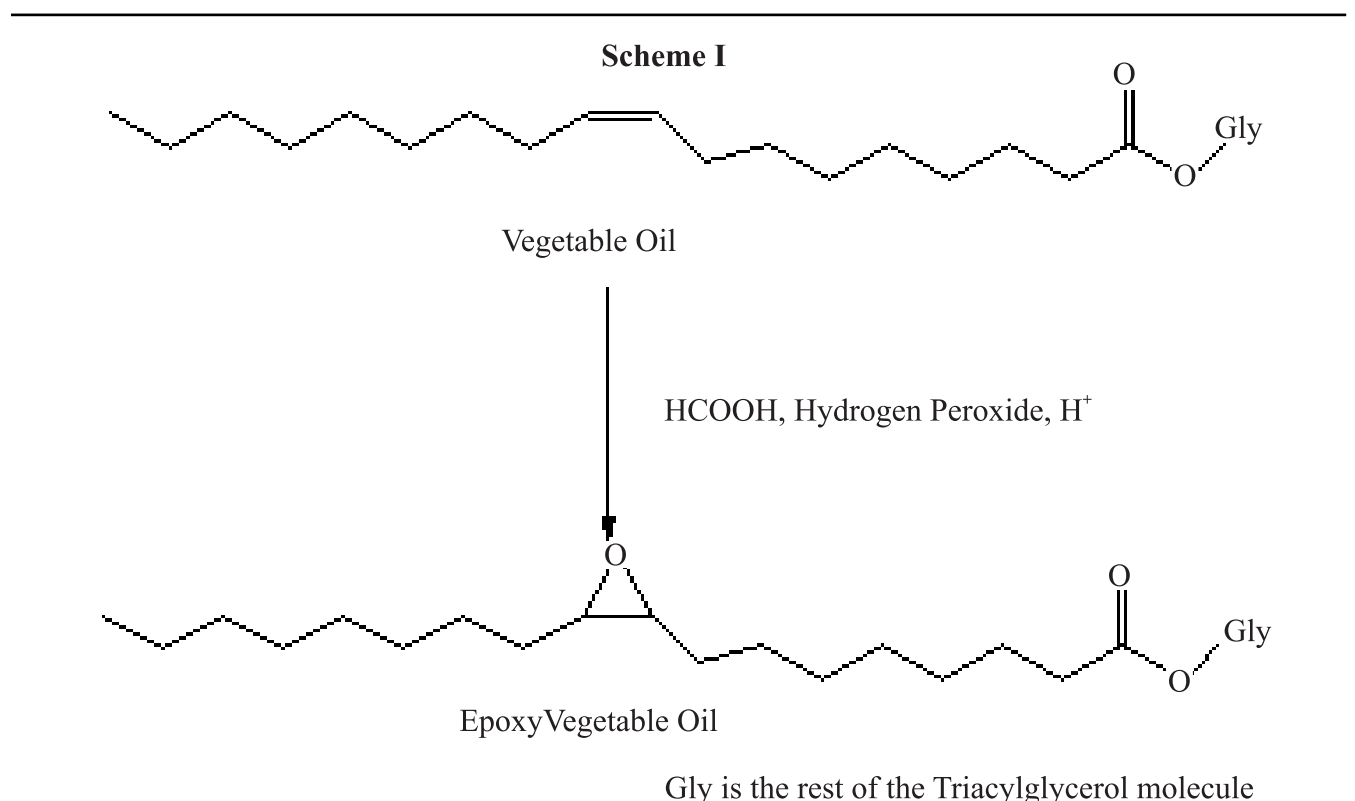
2.2 Extraction of oil

Plant material: *Semecarpus anacardium* L.f. 3 kg nuts were collected, shade dried and the nuts were directly percolated with cold petroleum ether 5-6 times, filtered and concentrated by vacuum evaporation. Again the powdered nuts were percolated with hot petroleum ether 5-6 times, filtered, and concentrated by vacuum evaporation. Both the cold and hot hexane extracts represent kernel oil and this oil can be either used for edible purpose or industrial purposes. The residual nut powder was subjected to both cold and hot acetone extraction and concentrated by vacuum evaporation to get. The above four concentrates were then fractionated using silica gel column with oil obtained from the fraction of HA (Hot acetone extract) 1-5 fractions, combined oil (named HA 5) was concentrated by vacuum evaporation and given for spectral analysis. Based on UV, FT-IR, ^{1}H NMR, ^{13}C NMR, MASS, HPLC, LCMS, GCMS, GC methods, it was found that it contains free fatty acids, triglycerides and others. Based on spectral data and its physicochemical properties *Semecarpus anacardium* L.f. nut residue oil was selected for synthesis of epoxy oil and its evaluation for Lubricant properties.

2.3 Epoxidation of bhallataka kernel residue oil

Epoxidation was carried out by varying the molar ratios of formic acid (2–3.5 mol) and hydrogen peroxide (4–10 mol). The general reaction for the epoxidation is shown in Scheme 1. In a typical optimized experiment, bhallataka oil (50 g, 0.17 mol) was placed in a three necked 250 mL round bottomed flask, equipped with a mechanical stirrer. A calculated amount of formic acid (3.94 mL, 0.102 mol) was charged into the flask and the mixture was stirred for 10–15 min. This was followed by the addition of a of 30 % hydrogen peroxide (mL, mol) using a dropping funnel, maintaining the temperature at 5–10 °C to prevent over heating of the system due to the exothermic nature of the epoxidation. Then the temperature was slowly raised to 60 °C and the reaction continued for 4 h. The course of the reaction was monitored by withdrawing aliquots of the reaction mixture at various time intervals. The samples were extracted with ethyl acetate, washed with water until they were acid free, and analyzed for their oxirane value. The epoxidized bhallataka oil with highest oxirane value was analyzed for iodine value and subjected to GC analysis. The structure of EBO was characterized by IR, ^{1}H NMR, ^{13}C NMR and ESI-MS spectral studies. After completion of the reaction, the solvent was removed using a rotary evaporator and the contents were extracted with ethyl acetate and washed with water until acid free. The organic layer was passed through sodium sulphate, concentrated and dried under reduced pressure (2–5 mm Hg) to afford epoxy bhallataka kernel oil. Epoxy oil methyl esters were prepared and analyzed by GC (Table 1)

Scheme I

Vegetable Oil

HCOOH, Hydrogen Peroxide, H⁺

EpoxyVegetable Oil

Gly is the rest of the Triacylglycerol molecule

Bhallataka oil: FT-IR (CHCl₃, cm⁻¹): 3007.22 (=C-H), 2925.38 (C-H), 2854.52 (C-H), 1745.89 (C=O), 1261.35 (C-OC(=O)), 1374.35, 1236.94, 1163.58 (C-O–C(=O)), 722.60. ¹HNMR (CDCl₃, ppm): 7.26-7.28, 5.24-5.42 (m, OCH-CH₂)₂), 4.12-4.18, 4.26-4.34 (dd, OCH₂-CH), 2.74-2.8, 2.28-2.2.36 (t,-CH₂-C=O), 1.98-2.08 (m, CH₂-CH=CH-), 1.56-1.68, (m, CH₂-CH₂-CO-), 1.20-1.42 (m, -CH₂-CH₃), 0.84-0.92 (t,-CH₂-CH₃). ¹³C NMR (CDCl₃, ppm): 173.152 (-COO-), 172.717, (130.11, 129.92, 129.74, 129.62, 128.0, 127.81) (-CH=CH-) 77.24, 76.99, 76.74, 68.02 (-CHOC=O), 34.11, 33.96, (31.86, 31.73, 31.47, 29.71, 29.57, 29.47, 29.43, 29.27, 29.22, 29.12, 27.14, 25.56, 24.81) (-CH₂).

Epoxidized oil: FTIR (CHCl₃, cm⁻¹): 2925.77, 2854.73, 1743.97, 1483.27, 1377.92, 1162.82, 1100.62, 723.57. ¹H NMR (CDCl₃, ppm): 5.24 (m, OCH-(CH2)2), (4.96-4.90, 4.32-4.24, 4.07-4.18) (dd, OCH₂-CH), 3.70-3.78, 2.28-2.37 (t,-CH₂-C=O), 2.22, (2.16-2.18, 2.12-2.14, (2.08-2.08, 2.28-2.04, 2.04-2.02), (1.18-1.68) (m, -CH₂-CH₃), (0.94-0.96, 0.96-0.96, 0.82-0.92) (t, -CH₂-CH₃). ¹³CNMR (CDCl₃,ppm): 173.13, 172.73, 130.09, 129.93, 129.63, 128.03, 127.83, 77.24, 76.94, 76.70, 68.86, 61.99, 34.15, 33.94, 31.85, 31.47, 29.76, 29.67, 29.56, 29.50, 29.44, 29.32, 29.30, 29.11, 29.0, 27.16, 25.58, 24.79, 22.66, 22.51, 14.08.

2.4 Transesterification of Epoxidized bhallataka Oil

Epoxidized bhallataka oil (5.0 g) and sodium methoxide (0.05 g, 1 wt %) were dissolved in 15 mL methanol were magnetically stirred at 60-65 C. The formation of methyl esters was monitored by TLC using solvent system n-hexane/ethyl acetate (90:10 v/v).After completion of the reaction, the solvent was removed *in vacuo* using a rotary evaporator and the resultant oil was dissolved in ethyl acetate. After washing with water the organic phase was dried (Na₂SO₄), filtered, concentrated *in vacuo*, and placed under vacuum to recover epoxy bhallataka fatty acid methyl esters (4.7 g).

2.5 Analysis

The fatty acid composition of the oil was analyzed by using gas chromatograph 6890N series of Agilent make using HP 1 column i.d. 0.25 mm, length 30 m. The injector and flame ionization detector were at 3000 C. The oven temperature was programmed at 1500 C for 2 min and then increased to 3000 C at 80 C/min. The carrier gas used was nitrogen at a flow rate of 1.5 mL/min. The GC-MS analysis were recorded using Agilent 6890 gas chromatograph with HP-1 MS capillary column (30 m×0.25 mm×0.5 μm) connected to

Agilent 5973 mass spectrophotometer at 70 eV (m/z 50-600; source at 2300 C and quadruple at 1500 C) in the EI mode. The iodine values of BO (*Semecarpus anacardium* oil), EBO (epoxy bhallataka oil), were determined using the AOCS Cd 1-25 standard method. The oxirane values were determined using the AOCS Cd 9-57 standard method. Quantitative analyses were always carried out in three replicates. ^{1}H NMR spectra were obtained using a Bruker ARX 400 Spectrometer 400, 500 MHz). ^{13}C NMR spectra were recorded in CDCl$_3$ on a Varian Spectrometer (400, 500 MHz). IR spectra were recorded on a perkin Elmer (model:Spectrum BX; Connecticut, USA)FT-IR Spectrometer neat as thin film.
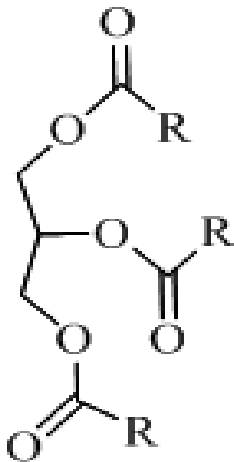
R (X:Y)=	16:0	18:0	18:1	18:2	20:0	20:1	22:0	24:0
Semecarpus anacardium oil	12.0	4.9	46.5	29.2	1.5	1.0	3.4	1.5

Fig. 1: Chemical structure of triglyceride and typical composition of *Semecarpus anacardium* oil in % (R (X:Y) = composition of the fatty acids; X = chain length of carbon atoms; Y= number of double bonds).

3 RESULTS & DISCUSSION

Triglyceride oil from *Semecarpus anacardium* is composed of (Fig.1) unsaturated fatty acids, oleic acid 46.6% lin- oleic acid 29.2% along with the saturated fatty acids Palmitic acid 12.0%, Stearic acid 4.9%, Archidic acid 1.5%, Paulinic acid 1.0%, Behinic acid 3.4%,Lignoceric acid 1.5% and 90.7 iodine value was epoxidised using peroxyformic acid generated *in situ* by reaction of formic acid with hydrogen peroxide in presence of sulfuric acid with 96 % of conversion. The reaction was monitored by analyzing the OVs. The maximum OV obtained for EBO is 3.7 % after 2 h.

The infrared spectrum of EBO epoxy ring opening reaction and the formation of diols did not occur in the epoxidation, as evident from the absence of absorption peak at 3300-3450 cm^{-1}. The ^{1}H NMR indicated almost complete conversion of the carbon–carbon double bonds by the absence of the characteristic peaks of olefinic and allylic hydrogen atoms at 5.3–5.4 and 1.95-2.05 ppm respectively. Peaks in the region of 2.8–3.1 ppm indicate the presence of epoxy group protons. The peak at 1.5 ppm corresponds to the presence of methylene group next to epoxy band while the peak at 1.7 ppm corresponds to methylene group sandwiched between two epoxy groups indicating the presence of diepoxy groups formed due to the epoxidation of linoleic acid. Absence of new peaks in the range 3.3–4.0 ppm indicated that hydrolysis and formation of diols did not occur during epoxidation. ^{13}C NMR spectrum of EBO showed almost complete disappearance of olefinic carbon atoms

between 120-140 ppm. In addition, carbon signals at 54-58 ppm indicated the presence of epoxy carbons. Peaks at 172 -173 ppm due to carbonyl carbons of triacylglycerol and 69 and 62 ppm for CH and CH_2 carbons of glycerol backbone confirm that glycerol fatty acid linkage is intact in the product. EBO was evaluated for lubricant properties namely, viscosity, viscosity index (VI), flash point, pour point, copper strip corrosion value and oxidation stability. Table 2 lists the physicochemical and lubricant properties of bhallataka oil, EBO and the lubricant properties of EBO were compared with epoxy oils of karanja, soybean and rape seed oils. Density and viscosity of epoxidised oils are more than their original oils due to their high molecular weight, more polar structure and stronger interactions between molecules (Adhvaryu and Erhan 2002).

Viscosity index of epoxidised oils is less compared to their virgin oils. These epoxy oils fall under group III category of base fluids as per API classification with their VI values well above 120. Pour point of epoxy oils is expected to be higher compared to their unconverted oils due to conversion of carbon–carbon double bonds to saturated epoxy group. Epoxy oils have exhibited higher flash points compared to their unconverted corresponding oils. With its high flash point indicating low volatility, EBO can be a potential candidate for high temperature applications. Corrosiveness of epoxy jatropha and soybean oils (1a) found to be good. Rotating bomb oxidation test was employed to evaluate the oxidation performance of epoxy jatropha and soybean oils and their unconverted oils. As expected oxidation stability improved in the case of the EBO as a result of the reduced number of carbon–carbon double bonds in the product. Thermal stability value is also high for EBO compared to BO.

Table 1 : Fatty acid composition of Bhallataka and epoxy Bhallataka fatty acid methyl esters

Fatty Acid	Composition (Wt %) of BO	Composition (Wt %) of EBO
Palmitic (16:0)	12.0	10.5
Stearic (18:0)	4.9	3.5
Oleic (18:1)	46.5	45.7
Linoleic (18:2)	29.2	24.5
Arachidic acid (20:0)	1.5	1.0
Pauliinic (20:1)	1.0	1.0
Behinic (22:0)	3.4	3.0
Lignoceric (24:0)	1.5	0.5

Table 2 : Physico-Chemical and lubricant properties of Epoxy Bhallataka (EBO)

Property		BO	EBO	EKO	ERO	ESBO
Density 15°C		0.898	0.921	0.982	0.985	0.991
Acid value		3.22	0.523	-	0.653	-
Oxirane value		-	3.79	4.2	4.9	6.6
Kinematic Viscosity	127.34	29.05	127.34	146.5	86.7	162.8
(cSt)	14.72	-	14.72	18.2	12.7	19.3
Viscosity Index		-	117	144	145	136
Pour Point (°C)		-	-6	9	-12	-3
Flash point (°C)		-	282	172	239	300
Copper strip corrosion		-	1a	1a	-	1a
DSC onset temperature (°C)		167	199	-	-	-
TGA onset temperature (°C)		319	372	-	-	-
Wear sacr dia (mm)		-	0.684	-	0.71	-
Weld load (Kgf)		-	180		70	180

BoO: Bhallataka oil; EBO: Epoxy bhallataka oil; EKO: Epoxy karnja oil; ERO: Epoxy rapeseed oil; ESBO: Epoxy soybean oil.

4 CONCLUSIONS

The epoxidation of bhallataka oil resulted in high reaction conversion of 96 %. The spectroscopic and gas chromatographic data indicate that nearly entire C-C unsaturation in bhallataka oil was converted to epoxy group. EBO exhibited better oxidative stability compared to that of virgin BO. In general, epoxidation improved all the lubricant properties except pour point. EBO exhibited comparable or better lubricant properties compared to EKO, ESBO and ERO. EBO could be a potential lubricant base stock for high temperature applications.

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[Contributed by Dr. K.N.PRASANNA RANI]

Enzymatic Modification of Menhaden Oil to Incorporate Caprylic and/or Stearic Acid

Menhaden oil was enzymatically modified with caprylic (8:0) and/or stearic acid (18:0) to produce structured lipids (SL) by Willet et al. with a goal to produce SL with high amounts of polyunsaturated fatty acids (PUFA), a low level of saturation, and a melting point of 25–35 C. Substrate (menhaden oil to acyl donor) molar ratios were 1:1, 1:3, and 1:5 for 8:0, and 1:1, 1:2, and 1:3 for 18:0. Enzyme load was 10% of the total weight of substrates. Time course study determined optimal time for maximum acyl donor incorporation. Linear interpolation estimated molar ratios that yielded SL with 20 or 30 mol% incorporation of 8:0 or 18:0. Enzymatic reactions were also conducted with molar ratios of menhaden oil to acyl donors:8:0:18:0 (1:1:3, 1:2:2, and 1:3:1). Lipases from *Candida antarctica* , Lipozyme® 435, and *Rhizomucor miehei* , Lipozyme® RM IM (Novozymes North America, Inc., Franklinton, NC, USA), were compared for all reactions [**J. Amer. Oil. Chem. Soc. 96, 761-775 (2019)**]. Total and *sn* -2 fatty acid compositions, triacylglycerol (TAG) molecular species, thermal behavior, volatile lipid oxidation products, solid fat contents, and oxidative stability were compared. When 8:0 was the acyl donor, the 1:3.03 and 1:4.58 ratios resulted in incorporation of 20 and 30 mol% 8:0, respectively. With 18:0 as the acyl donor, the 1:1.32 and 1:2.41 ratios led to incorporation of 20 and 30 mol% 18:0, respectively. The 1:3:1 ratio SL had a crystallization onset (C_0) of 15.3 °C and a melting completion (M_c) of 33.1 °C. The physicochemical properties of these SL suggest that some may be useful in formulating food products such as margarines and spreads.

The Effect of Branched-Chain Fatty Acid Alkyl Esters on the Cold-Flow Properties of Biodiesel

Biodiesel (fatty acid methyl esters [FAME]) is produced from various fats, oils, and greases (FOG) using catalytic transesterification with methanol. These fuels have poor cold-flow properties depending on the fatty acid (FA) composition of the parent FOG. Improving the cold-flow properties of biodiesel will enhance its prospects for use during cooler months in moderate temperature climates. This work by Dunn et al. is a study on the use of skeletally branched-chain alkyl esters (BCAE) composed of the isopropyl, *n* -butyl, and 2-ethylhexyl esters of iso-oleic acid isomers (iPr-iOL, nBu-iOL, and 2EH-iOL). These BCAE additives were tested in blends with linear-FAME (L-FAME) derived from soybean oil (SME), lard (LME), tallow (TME), and sewage scum grease (SGME) [**J. Amer. Oil Chem. Soc. 96, 805-823 (2019)**]. Binary L-FAME/SME admixtures were also studied. Admixtures were tested for the effects of the additives on cloud point (CP), pour point (PP), and kinematic viscosities at standard ($v^{40} = 40$ C) and low temperatures (T_L) = CP + 5 C (v^1). Although the BCAE additives were more effective than SME, relatively large additive concentrations (y_{Add}) were needed to depress CP and PP by more than 2 C. Admixtures with high concentrations of BCAE additive had $v^{40} > 6.0$ mm^2 s^{-1}, the maximum limit in ASTM fuel specification D 6751. While the iPr-iOL and nBu-iOL additives may be blended at concentrations up to $y_{Add} = 0.50$, 2EH-iOL should not exceed $y_{Add} = 0.28$ in LME, 0.31 in SGME, 0.35 in TME, or 0.41 in SME to avoid driving the admixture out of specification. Some anomalies observed in the results at low y_{Add} for SGME/BCAE admixtures were speculated to have been affected by the low-temperature rheology of SGME.

Renewable Poly(Thioether-Ester)s from Fatty Acid Derivatives via Thiol-Ene Photopolymerization

Partially bio-based poly(thioether-ester)s were prepared in high conversion from thiol-ene photopolymerization of fatty dienes with dithiols utilizing mild, solventless reaction conditions. Moser et al. synthesized fatty dienes by esterification of 9-decenoic acid, a terminally unsaturated medium-chain fatty acid that can be obtained from ethenolysis of oleic acid, with ethylene glycol and 9-decen-1-ol to yield bio-based

dienoic monomers amenable to subsequent thiol-ene polymerization. Polycondensation with 1,2-ethanedithiol (EDT) and 1,3-propanedithiol (PDT) gave a series of semicrystalline poly(thioether-ester)s with degrees of polymerization that ranged from 29 to 85, polydispersity indices between 2.81 and 4.38, and glass transitions from −36.8 to −25.7 C. The polymers were elastic at room temperature, with EDT-linked materials exhibiting greater elasticity than the corresponding PDT-linked polymers. All polymers were thermally stable below 320 C, with 10% mass loss (T_{10}) occurring above 338 C [**J. Amer. Oil Chem. Soc. 96, 825-837 (2019)**]. Enthalpies of fusion increased with higher relative crystallinity and were greater than the corresponding enthalpies of crystallization. The polymers were soluble in nonpolar solvents such as chloroform and THF but resisted dissolution in more polar solvents with dielectric constants above 10. Furthermore, the polymers were susceptible to acidic hydrolysis but resisted basic hydrolysis at room temperature.

Development and Application of a Rheological Method to Investigate Crystallization of Palm Oil

Structuring of fatty products is important in producing palatable food products. Saturated fat (SAFA) crystals are needed to bring structure to many products (such as bakery or confectionery). In a product control of the structure by fat nucleation and crystallization, it is important to deliver the correct performance. Many techniques only work on quiescent systems and give limited information about the sheared systems that are generally found in industrial production of products. This article presents a novel rheological technique that can be used to probe crystallization and network structure under sheared conditions [**J. Amer. Oil Chem. Soc. 96, 865-876 (2019)**]. The results show that crystallization of palm oil can be divided into different key stages. These result from initial nucleation, structuring by the crystals, polymorphic transformation, further structure building, and then subsequent relaxation. Significant postcrystallization (sintering) events occur over at

least a day. It is seen that the shear rate leads to possibilities for crystallization control. Higher shear gives a reduction in network strength (as measured by G′) of the initial crystal network. However, after longer posthardening, results are very similar. This work enables the development of a fast tool that can be used to monitor structure formation in fats and reveals the relative importance of the nucleation−crystallization and postcrystallization events in sheared systems.

Solvent - Free Enzymatic Synthesis of 1-*o* Galloylglycerol Optimized by the Taguchi Method

Gallic acid (GA) and its lipophilic forms, alkyl gallates, have been widely used in several industrial fields as antioxidants. However, the potential harmful effects of alkyl gallates, such as estrogenic effects, limit their application and raise safety concerns. The glycerol ester of GA, 1-*o*-galloylglycerol (GG), has not been reported to cause adverse health effects. Owing to the steric and electron-donating effects of GA, lipase-catalyzed synthesis of GG has not been successfully achieved. In this work by Zhang et al. glycerol ester of GA, GG, was successfully synthesized for the first time by the enzymatic transesterification of glycerol and *n*-propyl gallate (PG). GG was synthesized with an immobilized and commercially available food-grade lipase (Lipozyme® 435) under solvent-free (no extra solvent) conditions at atmospheric pressure and nitrogen flow. The effects of the reaction conditions, including the reaction temperature, substrate molar ratio, reaction time, and enzyme load, were optimized using the Taguchi method and regression analysis [**J. Amer. Oil Chem. Soc. 96, 877-889 (2019)**]. The structure of the product was elucidated using Fourier-transform infrared spectroscopy (FT-IR), electrospray ionization high-resolution accurate-mass tandem mass spectrometry (ESI-HRAM-MS/MS), and 1D and 2D nuclear magnetic resonance spectroscopy (NMR). Under the optimal conditions, GG was synthesized in 67.1 ± 1.9% yield at 50 C, 25:1 (glycerol:PG) substrate molar ratio, 120 hours, and 23.8% enzyme load relative to the total weight of

the substrates.

Crystallization of Cocoa Butter in Cocoa Powder Cocoa powder quality is determined by its color, flavor, dispersion, and flow properties, which can be controlled via tempering. Design of a cocoa powder tempering profile, however, requires that the mechanism of cocoa butter crystallization in cocoa powder be fully understood. A detailed study of crystallization of cocoa butter by Palmeiri et al, low-fat (8–12%) and high-fat (20–24%) cocoas were sourced from two commercial manufacturers at varying degrees of alkalization and compared with two commercial cocoa butters. Unrefined paired cocoa powders and cocoa butters sampled from the hydraulic press were also evaluated. Isothermal crystallization kinetics and polymorphism of cocoa powders and cocoa butters were compared at 18, 21, and 24 C using a direct time-domain nuclear magnetic resonance method, differential scanning calorimetry, and x-ray diffraction. Crystallization was also studied under dynamic tumbling conditions. It was found that cocoa butter in cocoa powder was nucleated by the cocoa powder matrix and transitioned to higher-stability polymorphs more rapidly than bulk cocoa butters. High-fat cocoas also exhibited enhanced crystallization kinetics relative to low-fat cocoas, showing that differences in the cocoa microstructure may influence crystallization behavior. Notably, alkalization did not significantly affect the crystallization behavior of most cocoa powders [**J. Amer. Oil Chem. Soc. 96, 911-926 (2019)**]. Finally, it was found that tumbling conditions led to crystallization of βV and that caking, especially of high-fat cocoas, could be reduced by a static low-temperature hold step prior to tumbling. Overall, these results demonstrated that crystallization of cocoa butter in cocoa powder is influenced both by the intrinsic attributes of the cocoa powder as well as the conditions of the tempering process.

Enzymatic Production of Diacylglycerols from High-Acid Soybean Oil
In this study by Zhong et al., high-acid soybean oil, with acid values (Av) ranging from 10 to 50, was enzymatically deacidified for diacylglycerol (DAG) production. The effects of glycerol amounts were studied intensively. The glycerol amount could be calculated theoretically based on the Av of the raw oil (1 mol glycerol with 2 mol oleic acid to form 1 mol DAG, and 1 mol glycerol with 2 mol soybean oil to form 3 mol DAG). A total of 60–62% of DAG could be obtained and the free fatty acid (FFA) content was reduced to 0.36–0.66%. Increased glycerol did not lead to DAG content improvement. However, the glycerol amount based on just the deacidification theoretical calculation (1 mol glycerol with 2 mol oleic acid to form 1 mol DAG) was not feasible to reduce the FFA content [**J. Amer. Oil Chem. Soc. 96, 967-974 (2019)**]. Moreover, Novozym 435 was rather stable in the present reaction procedure, no loss of activity was observed after 10 consecutive uses.

Differential Scanning Calorimetric Study of Solidification Behavior of Monoacylglycerols to Investigate the Cold-Flow Properties of Biodiesel

Monoacylglycerols (MAG) are impurities present in biodiesel as a result of incomplete reactions. MAG often solidify in biodiesel even at room temperature because of their high melting points. This worsens the cold-flow properties such as the cloud point and pour point. We hypothesized that several types of MAG solidify simultaneously; therefore, in a detailed study on solidifaication behavior of monoacyl glycerols, Seniorita et al. performed differential scanning calorimetry of binary mixtures of MAG to elucidate their interactions during solidification. Three thermodynamic formulas were then applied to the experimental results: (1) non-solid-solution, (2) solid-solution, and (3) compound formation models. Binary mixtures of MAG showed complicated liquidus curves with multiple upward convex shapes, with which only the compound formation model fitted well. This model was applied to multicomponent mixtures that consisted of MAG and fatty acid methyl esters (FAME) as surrogate biodiesel fuels. We confirmed that the model still worked well. The results show that the compound formation model has good potential for

predicting the cold-flow properties of biodiesel [**J. Amer. Oil Chem. Soc. 96, 979-987 (2019)**].

Tin Content Is a Possible Marker to Discriminate Argan Oil Against Olive, Sesame, Mustard, Corn, Peanut, and Sunflower Oils

Argan oil occupies an important position in the pharmaceutical, cosmetic, and food domains. Because of its elevated price, argan oil is subjected to adulteration practices by industrial or commercial actors eager to increase profit margins. Therefore, methods to ascertain argan oil authenticity are actively looked for. The use of argan oil elements as authenticity markers has been evaluated. To identify distinctive markers of argan oil allowing the detection of adulteration, the element content of seven pairs of vegetable edible oils is analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). For each pair, a plant is grown in Morocco and the other in a different country. Content of 12 metals in the resulting vegetable oil is determined and results are interpreted taking into account the soil element content. This study by Mohammed et al. shows that soil element content frequently influences the oil element content but argan oil, which is necessarily prepared from roasted argan kernels, represents a special case since its tin content is much higher than in any other oils. Tin content is a useful marker to characterize argan oil and can be used to certify its authenticity [**Eur. J. Lipid Sci. Technol. 121, 201800180 (2019)**].

Supercritical CO2 Extraction of Waste Citrus Seeds : Chemical Composition, Nutritional and Biological Properties of Edible Fixed Oils

Seeds of *Citrus* plants (Rutaceae), an major agro-industrial waste, are a potential source of valuable by-products. The chemical composition, the antioxidant profile, and the biological/nutritional properties of fixed oils (SFE oils) obtained by supercritical CO_2 extraction (at 300 bar and 40 C) from seeds of mandarin (*Citrus reticulata*), lemon (*Citrus limon*), and grapefruit (*Citrus paradisi*), discarded by a local agro-alimentary industry are studied. The yields and compositions of SFE oils are compared to oils

obtained by *n* -hexane extraction of *Citrus* seeds in a Soxhlet apparatus (SoxE oils). Linoleic (35–42%), oleic (22–28%), palmitic (21–25%), α-linolenic (4–10%), and stearic (4–7%) are the main oil fatty acids, while monolinolein and dilinolein derivatives represent the main triacylglycerols in SFE oils, determined by GC-FID and HPLC-DAD/ELSD techniques [**Eur. J. Lipid Sci. Technol. 121, 201800502 (2019)**]. *Citrus* SFE oils show lower yields than SoxE oils but similar chemical profiles. Principal components analysis applied to fatty acid and triacylglycerol data indicates that the oils from different seeds are tightly clustered. Moreover, SFE oils show radical scavenging activities (ABTS assays), an inhibitory effect on the growth of murine B16F10 melanoma cells and on the mushroom tyrosinase activity. *Citrus* SFE oils and de-coated seeds are also evaluated for their attractant effect on the Mediterranean fruit fly *Ceratitis capitata* by behavioral assays. The results qualify *Citrus* SFE oils as a potential natural, environmentally-friendly, resource for food/pharmaceutical applications.

Rose Hip Seed Oil: Methods of Extraction and Chemical Composition

Recently, there has been growing interest in the use of uncommon plant oils in the food and cosmetic industries. Oils obtained from *Rosa canina* L. and *R. rubiginosa* L. seeds are widespread on the market and recommended for pharmaceutical, cosmetic, and nutritional purposes. Both these oils are quite well investigated. However, *Rosa* L. genus includes numerous other species bearing fruits (hips) with seeds rich in active compounds. These rose species may also be a source of oil valuable for purposes above mentioned. Thus recent literature relating to rosehip seed oils, its extraction methods and composition are summarized by Dabrowska et al. to provide an overview of the published data on this subject. The goal of this article is to deliver necessary background with references for an up-to-date perspective of different rose species' seed oils, to review methods for their isolation, and thereby to compare oil extraction yield and composition [**Eur. J. Lipid Sci. Technol. 121,**

201800440 (2019)].

Cardanol-Based Epoxy Monomers for High Thermal Properties Thermosets

In this work, epoxy-anhydride networks are synthesized by Mora et al., from a new product of Cardolite Corporation: the Cardolite GX-2551 epoxy monomer. Due to the complexity of the GX-2551 structure, an NMR study is performed first to characterize this new commercial product. This epoxy monomer is then reacted with an anhydride (MHHPA) to form polyepoxide thermosets. After curing, dynamic mechanical and thermal analyses are performed for the different thermosets, and then the results are compared to each other **[Eur. J. Lipid Sci. Technol. 121, 201800421 (2019)].**

Hydroxylation and hexanoylation of epoxidized waste cooking oil and epoxidized waste cooking oil methyl esters: Process optimization and physico-chemical characterization

A novel process for the synthesis of biodegradable bio-lubricant basestocks from epoxidized waste cooking oil (WCO) and waste cooking oil fatty acid methyl ester (WCOFAME) was proposed by Borugadda and Goud. The synthesis process involved two steps, during the first step, epoxidized WCO, WCOFAME were hydroxylated (ring opening) in the presence of alcohol followed by functionalization of anhydride groups into resultant hydroxyl group. Hydroxylation of epoxidized WCO and WCOFAME was carried out with various alcohols such as methanol, 2-Propanol, 1-Butanol and 2-Ethyl hexanol (2-EH) in presence of homogeneous (sulfuric acid) and heterogeneous (ion exchange resin (IR-120)) acid catalysts. During the hydroxylation reaction, two different approaches (sequential addition and pre-mix addition) were attempted in adding the reactants (catalyst, alcohol) to epoxides. Both the approaches were studied thoroughly and concluded that outcomes of the pre-mix addition were best in terms of product conversion (99.5%), reaction time (30 min and 15 min) than the sequential addition. Similarly, hexanoylation was carried out in the presence of hexanoic anhydride; cationic ion exchange resin (Amberlyst-15) was used as a strong

acidic catalyst (3 wt.%). After each reaction, products were identified and confirmed by oxirane analysis (titrimetric technique) and spectral analysis (FTIR, ^{13}C NMR). Significant physico-chemical properties (pour point, thermo-oxidative stability, rheology, tribology and biodegradability) of the hydroxylated and hexanoylated WCO, WCOFAME was found to be −14.93 C , −28.45 C, −13.97 C, and −27.15 C after the structural modifications and the biodegradability of the prepared bio-lubricant basestocks contributed 93.6% and 90.8% for hexanoylated WCO, WCOFAME **[Ind. crops and Products, 133, 151-159].**

Synthesis and characterization of a novel tri-functional bio-based methacrylate prepolymer from castor oil and its application in UV-curable coatings

A novel tri-functional castor oil-based methacrylate prepolymer (MCOG) was developed by mercapto castor oil (MCO) and glycidyl methacrylate (GMA) in this study through a two-step method by Liang et al. Primarily, the mercapto castor oil (MCO) was prepared through thiol-ene reaction of castor oil and mercaptoacetic acid, and subsequently an esterification reaction based on above product and glycidyl methacrylate (GMA) was conducted. FT-IR and ^{1}H NMR spectra collectively revealed that MCOG was successfully synthesized. As a dominant component, MCOG was formulated with other additives including a reactive diluent pentaerythritol tri-acrylate (PETA), a photo-initiator (TPO) and another self-made polyurethane acylate prepolymers (B-215) and cured under UV irradiations. UV-curing kinetics of the MCOG/PETA/B-215 film was detailly investigated by tracing the ATR-IR spectroscopy and gel content and it demonstrated that the cured films had more than 95% C-C double bond conversion. Moreover, dynamic mechanical property, thermal stability and mechanical property of the cured films were respectively determined by dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA) and tensile measurement. DMA testified that with the increasing of B-215 content, storage modulus, cross-linking density of the cured films

dropped, whereas the corresponding glass transition temperatures (*Tg*) increased. TGA showed that the maximum thermal decomposition temperatures were all above 460 C. Tensile tests indicated that the better tensile strength was obtained with the content of 20% of the B-215 in the cured film. Additionally, transparency and flexibility of the cured films were respectively analyzed by digital image and scanning electron microscopy (SEM). Besides, these cured films displayed high pencil hardness (5H–6H) and excellent resistance to acidic and alkali solutions **[Ind. crops and Products, 135, 170-178].**

Palm oil-based biodiesel synthesis by radiation-induced kenaf catalyst packed in a continuous flow system
An efficient bio-based heterogeneous catalyst for biodiesel production was successfully fabricated by Zabaruddin et al. by radiation-induced graft polymerization of 4-vinylbenzylchloride (VBC) followed by quaternary amination of trimethylamine (TMA) and ion-exchange with aqueous sodium hydroxide onto kenaf bast fiber using electron beam irradiation at a dose of 150 kGy. The produced catalyst was characterized by FESEM–EDX, CHNS, ATR-FTIR, TGA and XRD analyses. In this study, the continuous catalytic transesterification of triolein/ethanol in a bench-scale packed bed reactor (PBR) was designed and tested. The reaction process was focused at room temperature, different residence times from 1 min to 4 min and a molar ratio of triolein/ethanol (1:50). Besides, study on the transesterification of palm oil with ethanol under optimized conditions for maximum conversion of triolein to ethyl oleate (residence time of 3 min, LHSV = 8 h^{-1}, short chain 150kGy catalyst) with temperature fixed at room temperature (~25 C) has been carried out [Ind. crops and Products, 136, 102-109]. The extracted ethyl oleate was analyzed by HPLC and ATR-FTIR. The results found that the continuous flow system has a great potential for producing ethyl ester to be used as biodiesel and it is possible to generate 100% biodiesel with high purity from palm oil using radiation-induced kenaf catalyst.

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