Recent Developments in Palm-based Lubricants

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INTRODUCTION

Lubricants are used to reduce friction, wear and heat between contacting surfaces in relative motion (Bart *et al*., 2013a). They can be classified based on physical appearance, *i.e.* solid, liquid or semi-solid. Liquid lubricants can be derived from petroleum, vegetable, animal or synthetic oils. Grease is a semi-solid material in which the liquid fraction is suspended in a solid matrix of thickener and additives. A solid lubricant is a solid material with a film comprising inorganic or organic compounds such as graphite, molybdenum disulphide and cadmium disulphide (Mobarak *et al*., 2014).

Lubricants are used in various industries such as manufacturing, commercial transport and consumer automobiles, generally divided into automotive and industrial applications. Examples of automotive lubricants include heavy-duty motor oil, passenger car motor oil, automotive gear oil, tractor hydraulic fluid and automotive transmission fluid. In industrial applications, lubricants are utilised as hydraulic fluids, metal working fluids, grease, general industrial oils (*e.g.* industrial gear oils, turbine oils, compressor and refrigeration fluids) as well as process oils (*e.g.* transformer oils, rubber oils, white oils and printing inks).

Formulation of lubricants uses one or more base fluids which could account for more than 95% as the major component, and these fluids can be categorised as mineral oils, synthetic hydrocarbons, plant-based oils or other synthetic fluids such as esters (Pettersson, 2007; Abdulbari *et al*., 2015). Base oils greatly determine the overall properties of a lubricant which is often formulated with a variety of additives ranging from 1% as in simple compressor oils and up to 30% as in metal working fluids and gear oils (Mang and Dresel, 2007). Additives such as antioxidants, viscosity modifiers, anti-wear agents and pour point depressants are employed to improve lubrication by modifying the properties of the base oil and/or those of the metal surfaces in order to meet the performance requirements of lubricant applications (*Figure 1*) (Bart *et al*., 2013b). Interest in biolubricants is emerging as accidental and usage losses of some mineral and synthetic lubricants can lead to ecological disasters in environmentally sensitive areas such as agriculture, forestry, mining, construction, waterways and harbors (García-Zapateiro *et al*., 2013). To date, biolubricants still comprise a narrow segment of less than 1% of the finished lubricant market globally (Kline, 2014). However, they are finding their way into applications such as metalworking fluids, food industry lubricants, biodegradable grease, agricultural equipment lubricants and others (Syaima *et al*., 2015).

PALM-BASED FEEDSTOCK FOR BIOLUBRICANTS

Base stocks used in biolubricants tend to be non-toxic and biodegradable. Vegetable oils are one of the most commonly used biodegradable lubricant base stocks other than low molecular weight polyalphaolefins (PAO), polyalkylene glycols (PAG), dibasic acid esters and polyol esters (Nagendramma and Kaul, 2012). Generally, vegetable oils have been known to have low toxicity, low volatility, high flash point, high viscosity index and good anti-corrosion properties, all of which are ideal for biolubricants (Mobarak *et al*., 2014). Various types of plant-based/vegetable oils have been employed as biolubricants, for instance, coconut, castor, canola, palm, sunflower, soyabean and *Jatropha curcas* oils (Soni and Agarwal, 2014).

The oil palm fruit is a unique crop in that various palm oil fractions with distinctive properties and characteristics can be utilised as feedstock for biolubricants, either as neat oil or subject to further oleochemical derivatisation. From the mesocarp of the palm fruit,

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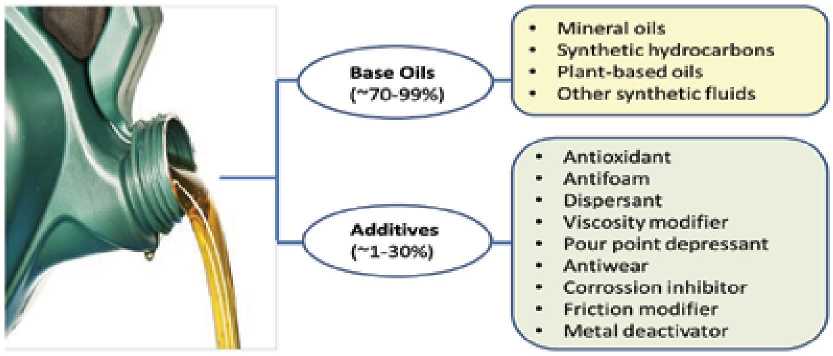

Figure 1. General composition of a lubricant formulation.

crude palm oil (CPO) is obtained and further refined to refined, bleached and deodorised palm oil (RBD PO), along with its by-product, namely palm fatty acid distillate (PFAD). PFAD consists of free fatty acids from the physical refining process of CPO, producing at around 4%-5% yield. Refined palm oil is then fractionated into a liquid fraction, namely palm olein (POo), and a solid fraction which is palm stearin (POs). There are two major grades of POo from the refinery. Standard olein is the product of single fractionation and has an iodine value of about 56 – 59 whereas super olein which has a higher iodine value of 60 and above is also known as double-fractionated olein. On the other hand, palm kernel oil (PKO) is obtained from the kernel of the oil palm fruit. Plant-based oils are natural esters consisting of triacylglycerols (also known as triglycerides) which are glycerol esters of three fatty acid chains with variations in length of the hydrocarbon chains and in degree of unsaturation. The fatty acid composition of oils and fats obtained from the mesocarp of the oil palm fruit differs significantly from that of the kernel oils as shown in *Table 1*. Palmitic acid (C16:0) and oleic acid (C18:1) are the major fatty acids in the palm fractions from CPO whereas short- and medium-chain fatty acids (C8:0 to C14:0) constitute the major portion for PKO. Being rich sources of particular fatty acids, these oils and fats are excellent feedstock for oleochemicals to obtain different cuts of fatty acids for various applications. The uses of palm-based feedstocks as biolubricants have been reported in some recent studies.

RBD PKO and POo showed an enhanced extrusion load greater than mineral oil-based lubricants, and no severe wear on the product surface was observed in a lubrication test for cold extrusion processes (Nurul *et al*., 2016). This indicates that PKO and POo can be considered as replacements for mineral oil-based lubricants to be used in metal-forming processes in the industry, such as metal casting, metal rolling, metal forging, metal extrusion, metal drawing, sheet metal and other related manufacturing processes.

In addition, the potential of double-fractionated palm oil (DFPO) as a biolubricant was examined by using aluminum pins and a SKD 11 (alloy tool steel) disc with a pin-on-disk tribo-tester to investigate its friction and wear characteristics (Nuraliza and Syahrullail, 2016). DFPO as a base lubricant is better for mechanical applications to overcome friction and wear problems that occur between metal-to-metal contact, as it showed best overall performance in terms of wear, coefficient of friction and viscosity in a study comparing it to hydraulic oil and engine oil (SAE 40) as references. The lowest value for the coefficient of friction was observed for DFPO when 50 N and 100 N loads were applied throughout the 1 hr operation time, presumably because the fatty acid component of such a lubricant forms multi and mono layers on the surfaces of the rubbing zone and makes a stable film which prevents direct contact between the surfaces.

In another report by Golshokouh *et al*. (2014), PFAD showed better anti-friction and anti-wear ability and better tribological characteristics compared to engine and hydraulic oils under the different applied loads and working temperatures tested using a four-ball tribotester. The findings from the study suggest that PFAD may be a viable alternative to mineral lubricant oils.

CHEMICAL MODIFICATION AND DERIVATISATION OF PALM-BASED FEEDSTOCKS

Plant-based oils are the major source of biodegradable base stock owing to their economic and environmental-friendly characteristics as well as the effective lubricity performance for applications with low thermal stress, such as when used in total loss applications like in mold release, chain saw oils and track lubricants (Wagner *et al*., 2001). However, their thermal, oxidation and hydrolytic stability are limited despite the poor low temperature performance. In order to improve the inferior properties of vegetable oils to be used as lubricants, chemical modifications of the triglycerides are carried out, *e.g.* by transesterification/esterification, branching, epoxidation and

TABLE 1. FATTY ACID COMPOSITION (FAC) OF PALM-BASED LUBRICANT FEEDSTOCKS

	Palm oil[a]	Palm olein[b]	Super olein[c]	Palm stearin[d]	PFAD[e]	Palm kernel oil[f]
IV*	50.4 – 53.7	56.0 – 59.1	60.1 – 67.5	27.8 – 45.1	46.3 – 57.6	16.2 – 19.2
FAC (%)**						
C6:0	-	-	-	-	-	0.1 – 0.5
C8:0	-	-	-	-	0.0 – 0.3	3.4 – 5.9
C10:0	-	-	-	-	0.0 – 0.2	3.3 – 4.4
C12:0	0.0 – 0.5	0.2 – 0.4	0.2 – 0.4	0.1 – 0.3	0.1 – 2.4	46.3 – 51.1
C14:0	0.9 – 1.5	0.9 – 1.2	0.9 – 1.1	1.1 – 1.7	0.9 – 1.6	14.3 – 16.8
C16:0	39.2 – 45.8	38.2 – 42.9	30.1 – 37.1	49.8 – 68.1	43.0 – 49.1	6.5 – 8.9
C16:1	0.0 – 0.4	0.1 – 0.3	0.2 – 0.4	<0.05 – 0.1	0.1 – 0.3	-
C18:0	3.7 – 5.4	3.7 – 4.8	3.2 – 4.3	3.9 – 5.6	4.0 – 4.5	1.6 – 2.6
C18:1	37.4 – 44.1	39.8 – 43.9	43.2 – 49.2	20.4 – 34.4	34.7 – 37.2	13.2 – 16.4
C18:2	8.7 – 12.5	10.4 – 12.7	10.7 – 15.0	5.0 – 8.9	8.5 – 9.7	2.2 – 3.4
C18:3	0.0 – 0.6	0.1 – 0.6	0.2 – 0.6	0.1 – 0.5	0.3 – 0.5	TR – 0.9
C20:0	0.0 – 0.5	0.2 – 0.6	0.0 – 0.4	0.3 – 0.6	0.0 – 0.4	
Saturated FA (%)	43.8 – 53.7	43.2 – 49.9	34.4 – 43.3	55.2 – 76.3	48.0 – 58.5	75.5 – 90.2
Unsaturated FA (%)	46.1 – 57.6	50.4 – 57.5	54.3 – 65.2	<25.5 – 43.9	43.6 – 47.7	15.4 – 20.7

Note: *IV - iodine value (I_2/100 g, Wijs); **Reported as wt% of methyl ester; FA - fatty acids; TR – trace.

1. Figures shaded in grey indicate the major fatty composition of the oil.
2. The identity characteristics of processed palm oil do not differ significantly from those of crude palm oil, with the exception of carotenoids which are destroyed during refininga.

Source: [a]MS 814: 2007; [b]MS 816: 2007; [c]*PORIM Technology* (1995); [d]MS 815: 2007; [e]Tay and Yusof (2009); [f]*PORIM Technology* (1986).

estolide formation, either on the carboxylic functional group or the hydrocarbon chain (McNutt and He, 2016). Most of the oleochemical transformations focus on the carboxylic groups rather than the latter.

Synthetic oleochemical esters are made predominantly by reacting mono- or poly-alcohols with one or more fatty acids, depending upon the required base fluid properties. Most of the synthetic esters are synthesised from petroleum-derived branched polyols such as neopentyl glycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PE). Vegetable oils are thermally sensitive due to the presence of hydrogen in the beta (β) position of the glycerol backbone in the triglycerides which tends to undergo elimination at high temperature (Cavalcante *et al*., 2014). The unsaturated compounds formed may undergo polymerisation which leads to increased viscosity and resulting in precipitates. Thus, synthetic esters, particularly polyol esters, are among one of the most interesting groups for biolubricant base stocks as this class of products offers extraordinary stability due to the absence of a secondary hydrogen in the β-position and the presence of a quaternary C-atom in the centre (Wagner *et al*., 2001). Examples of ester structures with and without the presence of β-hydrogen are illustrated in *Figure 2*.

Lubrication properties of palm oil and PKO TMP esters derived from transesterification of TMP with methyl esters of palm oil and PKO were reported by Yunus *et al*. (2004). Pour point of the synthesised esters was relatively high, between 4°C and -1°C due to the high content of saturated fatty acids, but it was improved to at least -33°C in high oleic palm oil TMP esters. The palm oil and PKO methyl ester-based TMP esters showed good potential as base stocks in biodegradable lubricant formulations as their lubrication properties such as viscosity, viscosity index, wear and friction properties are comparable to commercial hydraulic fluids. Notably, their oxidative stability is even more superior to that of high oleic vegetable oil.

Some of the fatty acids commonly utilised for synthetic esters can be obtained from palm-based oils, *e.g.* lauric acid (C12:0), palmitic acid (C16:0), stearic acid/isostearic acid (C18:0) and oleic acid (C18:1) (*Table 1*), through an oleochemical process. The properties of synthetic esters depend on the structure of the constituent fatty acids, *i.e.* the length of the fatty acid chain and the number and relative position of the unsaturated bonds. Saturated acids are more resistant to oxidation at high temperature but have high pour point properties due to their linear structure. On the other hand, polyunsaturated fatty acids exhibit low pour point but they tend to undergo oxidation and thermal degradation (Padmaja *et al*., 2012). Monounsaturated fatty acids such as oleic acid have been found to exhibit a good balance of low melting point with good thermo-oxidative stability and viscosity (Wagner *et al*., 2001; Nagendramma and Kaul, 2012).

Palm-based polyol esters which were characterised by higher oxidative and thermal stabilities have been reported to be useful as dielectric fluids (Raof *et al*., 2016), metal working fluids (Chang *et al*., 2015) and automotive engine oils (Zulkifli *et al*., 2013). TMP esters in particular which have the advantages of a wide viscosity range, high flash point and fire-resistant attributes are widely used in the lubricant industry (Chang *et al*., 2015). In addition, a palm-based ethylhexyl ester has been reported for use as a base oil in a synthetic drilling fluid formulation (Abdul Habib *et al.*, 2014). The high kinematic viscosity of the ethylhexyl ester gives better lubrication to the drilling fluid compared with other ester-based oils while its pour point (-15°C) and flash point (204°C) values are superior for the desired application.

Palm-based synthetic esters such as 2-ethylhexyl esters of lauric/palmitic/stearic acids and polyol esters, *e.g.* TMP oleate, C8-10 esters of TMP, NPG and PE oleates, are available commercially from OLEON, KLK Oleo and Emery Oleochemicals. The physico-chemical properties of the synthetic esters are shown in *Table 2* while their lubricant applications are presented in *Table 3*.

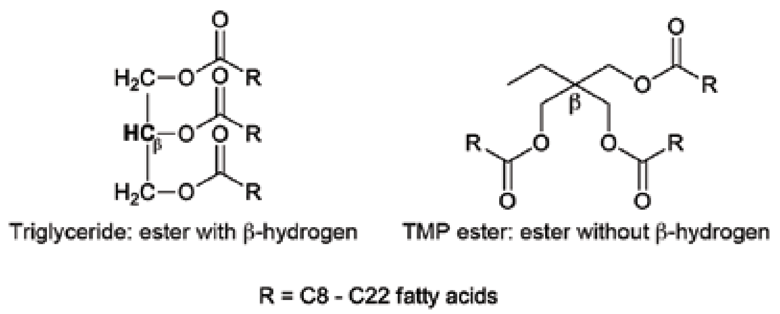

Figure 2. Illustration of esters with and without β-hydrogen.

Other than the transesterification process, various approaches for chemical derivatisation of oils or its oleochemicals on the olefinic group on the fatty acid chain or carboxylic head group manipulation to afford structurally-modified synthetic esters have been reported. Generally, modification of the alkene groups to other stable functional groups can improve oxidative stability while low temperature performance is enhanced by reducing the structural uniformity of the oil through attaching alkyl side chains (Salih *et al*., 2011).

Epoxidation of PKO alkyl esters followed by esterification with acid anhydrides was studied for application in green insulating fluid (Abdelmalik, 2014). The synthesised PKO-based branched alkyl esters have about four times lower viscosity than that of mineral insulating oil, suggesting that they can serve as more viable heat transfer and dissipation agents than the mineral oil. The physico-chemical properties of the esters implied that the derivatives could serve as effective dielectric coolants.

Furthermore, oleic acid-based esters have been studied extensively as they present better cold flow properties and lower pour point which make them interesting for the synthesis of liquid lubricants and for applications in cold climates (Cavalcante *et al*., 2014). Complex esters such as oleic acid triesters were synthesised by Salimon *et al*., through epoxidation of oleic acid followed by ring-opening branching strategies and esterification of carboxylic acid (Salimon *et al*., 2011a; b; 2012). The research findings suggest that increasing the chain length of the mid- and end-chain alkyl group gives a positive impact on the low temperature and anti-wear properties of ring-opening products as they create a steric barrier around the individual molecules and inhibit crystallisation, resulting in lower cloud and pour points. However, increasing chain length is detrimental to onset temperature property as longer chains are more susceptible to oxidative cleavage

TABLE 2. PHYSICO-CHEMICAL PROPERTIES OF SYNTHETIC ESTERS FOR FORMULATING LUBRICANTS

Property	Viscosity at 40°C, $mm^2 s^{-1}$	Viscosity at 100°C, $mm^2 s^{-1}$	Viscosity index	Pour point, °C	Cloud point, °C	Flash point, °C
Monoesters						
2-Ethylhexyllaurate	5	n.r.	n.r.	-30	<-10	170
2-Ethylhexylpalmitate	8.1	n.r.	n.r.	-3	<2	210
2-Ethylhexylstearate	9.1	n.r.	n.r.	7	<10	220
2-Ethylhexyloleate	8.2	n.r.	n.r.	-30	<-15	210
Polyol esters						
NPG-dioleate	24	5.9	207	<-21	-32	275
TMP-trioleate[a]	46	9.3	195	<-40	<-20	>300
TMP-trioleate[b]	68	12.5	190	<-45	-24	>300
PE-tetraoleate	65	14	185	-30	<-3	300
PE-monooleate	104	13.5	130	-27	<0	280

Note: n.r - not reported; [a] and [b] denote different specifications of the products.
Source: Oleon Radialube Product Brochure.

TABLE 3. LUBRICANT APPLICATIONS OF SYNTHETIC ESTERS

Application	HO	MWF	SRO	AP	CL	EO	GTO	Grease
Monoesters								
2-Ethylhexyl-C8-14-ester	x	x	-	-	-	-	-	-
2-Ethylhexyllaurate	-	-	x	-	-	-	-	-
2-Ethylhexylpalmitate	-	x	-	-	-	-	-	-
2-Ethylhexylstearate	-	x	-	-	-	-	-	-
2-Ethylhexyloleate	x	x	-	-	-	-	-	-
Polyol esters								
NPG-dioleate	x	-	x	x	-	-	-	-
NPG-C8-18-ester	-	-	x	-	-	-	-	-
TMP-C8-10-ester	x	-	-	-	x	x	x	x
TMP-oleate	x	x	x	-	-	-	-	x
PE-dioleate	x	-	-	-	-	-	x	-
PE-C8-10-ester	-	x	-	-	x	-	-	x

Note: HO - hydraulic oil, MWF - metal working fluid, SRO - steel rolling oil, AP - aluminium processing, CL - chain lubricant, EO - engine oil, GTO - gear and transmission oil.
Source: Emery Biolubricant Product Brochure.

than shorter chains (Salimon *et al*., 2011a; b). It was proposed that these oleic acid-based products may be usefully applied in a general purpose biolubricant such as chain saw machine oil, brake fluid and transmission oil.

In recent years, a new class of synthetic base oils known as estolides has garnered considerable interest as promising base stocks for biodegradable lubricants. Estolides is a class of esters formed when the carboxylic acid group of one fatty acid molecule forms an ester link with a hydroxyl group of a second fatty acid or at a site of unsaturation of another fatty acid (Cermak and Isbell, 2002; García-Zapateiro *et al*., 2013; Cermak *et al*., 2015). *Figure 3* shows examples of monoestolide products with ester links formed at unsaturation sites as in oleic estolide, and ester links formed at the hydroxyl groups of ricinoleic acid-based estolide. These higher molecular weight derivatives of fatty acids have been studied for various applications including as food emulsifiers, coatings, cosmetics (particularly for hair care products), pigment dispersants and plasticisers, apart from use in the lubricant industry (García-Zapateiro *et al*., 2013).

The reported work on estolide esters focused on two different types, namely, oleic-based estolide esters (Isbell *et al*., 2001) and saturated-capped oleic-based estolide esters (Cermak and Isbell, 2001). The latter type refers to estolides that have a saturated fatty acid (such as coconut fatty acid) as the last fatty acid to be added across the double bond during the oligomerisation reaction. Compared to triglycerides, secondary ester linkages of estolides are more resistant to hydrolysis (Cermak *et al*., 2015). Extensive research on the starting materials and the reaction conditions had afforded estolides with physical properties superior to those of vegetable and mineral oils (such as low pour point properties) in certain applications (Cermak and Isbell, 2002; 2015).

Commercially, estolides have been developed by Biosynthetic Technologies (Irvine, California) and manufactured using their patented technology that converts vegetable oils into high performance base oils with exceptional results in terms of oxidative stability, hydrolytic stability, volatility, biodegradability and renewable carbon content. Marketed under the brand name *Biosynthetic Base Oils*, the estolide products exhibit high viscosity index (173 for the product biosynthetic estolide SE7B), are fully miscible with Group I-V base oils and are readily soluble with a broad range of lubricant additives. These properties have enabled estolides to be utilised in a wide array of applications, including in passenger car motor oil, hydraulic fluid, grease, dielectric fluid, metalworking fluid as well as in various marine applications (Bredsguard, 2014).

In the context of palm-based feedstocks, PFAD, a relatively inexpensive by-product from the palm oil refinery, has been utilised to produce estolide for drilling fluid application. Referring to the patent EP3009492 A1 filed by a lubricant manufacturer (Jeon *et al*., 2016), the PFAD-derived estolide base stock demonstrates high flash point (>130°C), low pour point (-8°C) and is free of aromatics such as polyaromatic hydrocarbons (PAH). These properties show that PFAD-derived estolide has strong potential to be used in diesel-type drilling mud applications.

CURRENT STATUS AND FUTURE PROSPECTS

Global lubricant demand is projected to grow at less than 2% per year from 38.7 million tonnes in 2012 to reach 42.1 million tonnes by 2017. For biolubricants, Europe and the Americas consume an estimated 250 000 to 300 000 t per year accounting for 80% to 90% of the global supply, while Asia and the rest of the world account for the balance (Kline, 2014). Over 56% of the global biolubricant market volume in 2015 is attributed to automotive applications, apart from industrial applications (Grand View Research, 2016). Asia is the market leader for finished lubricant consumption in 2012 accounting for 43%, followed by North America (25%), Europe (17%), Africa and the Middle East (8%) and South America (7%) (Gill, 2014; Kline, 2014). However, the market for biolubricant finished products is very minor in the Asian region in spite of the fact that Asia is one of the major producers of their feedstock. The lack of sufficient regulatory mandates and the higher price of biolubricants compared with petroleum-based lubricants have been identified as the major limiting factors which explain the small market share of biolubricants in Asia (Markets and Markets, 2016).

Nonetheless, the Malaysian government is devoting efforts in promoting the development of biolubricants through the implementation of the Malaysia Plan. The 11th Malaysia Plan, which started at the beginning of 2016, focuses on enhancing the palm oil sector's productivity and sustainability, while expanding markets. As Malaysia is one of the world's largest basic oleochemical producers, the government has been encouraging the production of higher value-added oleochemical derivatives and bio-based chemicals through implementation of the Entry Point Project (EPP) 6 under the Palm Oil National Key Economic Area (NKEA) (Economic Transformation Programme, 2016). Since 2011, capital expenditure incentive grants have been disbursed under EPP 6 to facilitate companies that are interested in embarking further on palm oil downstream ventures (Lam, 2015). Biolubricants is one of the six key high value oleo derivatives that

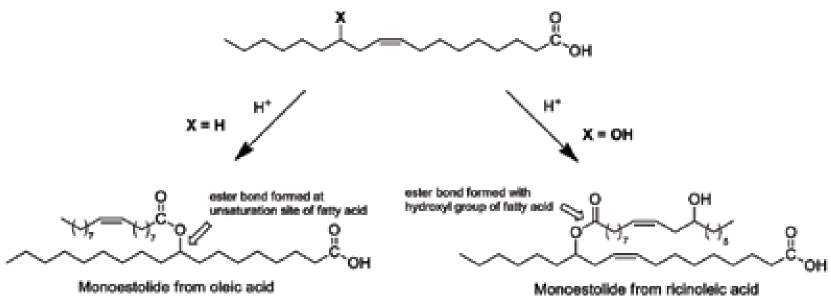

Figure 3. Examples of monoestolides from oleic acids and ricinoleic acids.

are given focus for development under this EPP, in addition to agrochemicals, surfactants, biopolyols, glycerol derivatives and bio-based chemicals.

Apart from environmental concerns, biolubricants have been sought after as an alternative to food grade lubricants. MPOB has developed a series of palm-based food-grade lubricant base fluids (Loh and Choo, 2006a) certified by the National Sanitation Foundation (NSF) as HX-1 ingredients for use in lubricants with incidental food contact (H-1) in and around food-processing areas. Palm-based food-grade industrial lubricants formulated with those base fluids and fortified with specialty additives for the production of spindle oil, hydraulic fluid and circulating oil applications have also been introduced (Loh and Choo, 2006b, c, d).

The global biolubricant market exceeded USD 2.0 billion in 2015 and is estimated to reach USD 3.15 billion by 2021, registering a CAGR of 6.3% between 2016 and 2021. The biolubricant market is expected to have significant growth in the next five years due to increasing penetration driven by the increase in supply of high performing and cost-competitive renewable source base oils, in the context of government regulations and standards, supported by industry interest in developing green formulations for various end-users (Grand View Research, 2016; Markets and Markets, 2016).

CONCLUSION

Palm-based feedstocks have been utilised for biolubricant applications in the form of neat oil or oleochemical derivatives such as polyol esters as base stock in formulated products. Palm-based oils are unique compared to other plant oils as oils with different fatty acid compositions can be obtained from the mesocarp and kernel of the palm fruit. Despite the fact that plant oil has the inherent characteristics of inadequate oxidation stability, poor low temperature properties and hydrolytic stability, it is still a feasible choice for lubricants for total loss applications. Chemical modifications of the triglycerides or its oleochemicals (fatty acids) lead to the development of synthetic esters and estolides with better physico-chemical properties to overcome the impediments of plant oils destined to be employed as high performance lubricants. Increasing awareness in biodegradability with regard to the use of lubricants in environmentally sensitive areas and in safety features important in food-grade applications has spurred the research and development of sustainable green chemicals such as palm-based products for biolubricants. Consumer acceptance of biolubricants depends greatly on their cost and performance in desired applications, and hence more efforts from research, development and commercialisation need to be exerted in this direction to enable sustainable growth for biolubricants in the future.

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