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INFLUENCE OF A LUBRICANT AUXILIARY FROM PALM OIL METHYL ESTERS ON THE PERFORMANCE OF PALM OLEIN-BASED FLUID

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ABSTRACT

The increasing demand to replace toxic petroleum products with non-toxic renewable sources has driven the use of environmental-friendly lubricating fluids, particularly vegetable oils with modified or enhanced lubricating properties. However, relatively little has been reported on the use of a plant oil-based lubricant auxiliary, e.g. *methyl esters, as an oil component for biolubricant manufacturing, and on the resulting lubricating characteristics. Hence, this article investigates the effect of the presence of methyl esters of palm oil (POME) as a lubricant auxiliary on the lubricating characteristics of palm olein-derived base fluids. Palm olein was fortified and homogenised with 1%, 10%, 20%, 30% and 40% POME, and the lubricating performance of each base fluid was compared with that of palm olein. Interestingly, the POME-fortified palm olein-derived base fluids were found comparable to, if not better than, the mother fluid (palm olein) in a couple of the properties studied, and some properties were superior to the required SAE standards/specification for commercial petroleum-based lubricants. The changes in lubricating properties were directly related to the proposed structural linkage of POME to the triglyceride molecules in palm olein.*

Keywords: palm olein, palm oil methyl esters, lubricant auxiliary, lubricating fluid.

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INTRODUCTION

Mineral-based or petroleum-based lubricants are detrimental to the environment, the ecosystem and human health as they are not easily biodegradable, are toxic and non-renewable. Due to the environment-unfriendliness of petroleum-based lubricants and the fast depletion of mineral oil, a keen search for vegetable oil-based lubricants has mushroomed in recent years with an increase in global environment awareness among the public. As a lubricant comprises 97% to 98% base fluid with 2% performance additives, the role of the base fluid in a lubricant is very important. The quality of a base fluid determines the performance of the lubricant formulated (Bunemann and Steverink, 2000). For better environment-friendliness, the present petroleum-based fluids can be replaced by either synthetic fluids or vegetable oils. As vegetable oils are found in abundance and are renewable, they are more economically and preferably used than synthetic fluids to substitute for the petroleum-derived base fluids.

Thermal stability and cold-temperature fluidity are the two desirable properties for a good lubricant base fluid. Bio-based fluids from vegetable oils such as soyabean, sunflower, canola and rapeseed oils often have superior viscosity indices, flash points, extreme pressure lubricity, good compatibility with additives and lower volatility than their petroleum counterparts (Honary, 2001). However, many vegetable oils are inferior in thermal oxidative stability due to their high content of unsaturated fatty acids, and in their cold-temperature fluidity due to the high melting points of their saturated fatty acids (Nagaoka and Ibuki, 2000; Erhan and Adhvaryu, 2002), thus making them uncompetitive

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TABLE 1. CONFIGURATION OF BASE FLUID BLENDS

Sample code	Pure olein	FG Base 1	FG Base 2	FG Base 3	FG Base 4	FG Base 5
Olein/POME (% wt)	100/0	99/1	90/10	80/20	70/30	60/40

Note: POME – palm oil methyl esters.

compared with their petroleum counterparts. These drawbacks can be overcome by chemical modification (Bisht *et al*., 2002; Hwang and Erhan, 2002; Cermak and Isbell, 2003; Erhan *et al*., 2003) of the fatty acid compositions, by incorporating additives (Wan Sani *et al*., 1998; Erhan and Adhvaryu, 2002; Cheenkachorn *et al*., 2003) to the oil, or by blending the monoester-based vegetable oils with mineral oil (Kaul *et al*., 1997). Another possibility is through genetic modification (Erhan and Adhvaryu, 2002). Several attempts made in the past have shown that the presence of a plant oil-based lubricant auxiliary such as methyl esters enhances the lubricating properties of a vegetable oil, but insightful investigation have not been accomplished.

Generally, palm olein has been explored (Dobbin and Wood, 1993; Cox *et al*., 1994; Wan Sani *et al*., 1998) as a potential base fluid to substitute petroleum-based fluids in lubricant formulation. This is because palm olein has moderate thermal oxidative stability and cold-temperature fluidity associated with its equal amounts of saturated and unsaturated fatty acids, making it potentially and suitably flexible enough to be formulated into intended bio-lubricants provided that some enhancement of its lubricating properties is made. The influence of methyl esters of palm oil (POME) on the lubricating properties of palm oil/palm olein has not yet been exploited, although a partial study on the addition of 5% of POME to palm olein has shown evidence of better performance (Maleque *et al*., 2000). Thus, this article examines how a lubricant auxiliary, POME, can affect the lubricating properties of palm olein, and gauges its potential as a substitute for petroleum-based fluids.

MATERIALS AND METHODS

Materials

Palm olein was obtained locally from palm oil refineries. The esters auxiliary, *i.e.* POME was synthesised via alkaline transesterification (Choo *et al*., 1990) of palm oil using sodium hydroxide (NaOH) and methanol. Commercial grade NaOH and methanol (98%) were obtained from Merck, whereas palm oil was obtained from a local palm oil mill.

Methods

Production of the base fluid blends was carried out in a multi-purpose mixer tank (5-litre capacity) by blending the required amount of palm olein and POME in different percentages (%, dry weight basis: 99:1, 90:10, 80:20, 70:30, 60:40) (*Table 1*). The mixer tank was equipped with a stirrer. The mixtures, *i.e.* palm olein and POME, were stirred vigorously at 100 rpm at room temperature for 10 min, then stored in the dark in sample bottles with sealed lids for use in the evaluation of their lubricating properties.

Analyses. The lubricating characteristics of the base fluid blends were measured according to the respective ASTM Test Methods: kinematic viscosity at 40ºC and 100ºC by an automated multi-range viscometer HVM472 (Walter Herzog, Germany) according to ASTM D445; viscosity index according to ASTM D2270; specific gravity at 15ºC by a digital density meter; pour point and cloud point by an automatic pour point/cloud point measuring apparatus (ISL CPP 97-2 Analyser) according to ASTM D97 and ASTM D2500, respectively; flash point measurement by a Pensky-Martens closed cup tester according to ASTM D93; moisture content by the Karl Fisher method according to ASTM D1744; rotating pressure vessel oxidative test (RPVOT) by a quantum oxidation tester (Tannas, USA) according to a modified ASTM D2272 under dry conditions; air release by an air release apparatus according to ASTM D3427; demulsibility test according to ASTM D1401; foaming characteristic according to ASTM D892; rust preventive test according to ASTM D665-A; copper strip corrosion according to ASTM D130; and extreme pressure (EP) by 4 ball test according to IP 239. All determinations were performed in triplicate, and the mean values were reported.

RESULTS AND DISCUSSION

Palm oil/palm olein is a mixture of the triglycerides of fatty acids ranging from C8 to C20 (*Table 2*). Palm oil is derived from the mesocarp of the fruit of the oil palm species, *Elaeis guineensis*, while palm olein is the liquid fraction obtained by fractionation of palm oil and has a triglyceride composition ranging from C44 to C56 (*Table 3*).

TABLE 2. FATTY ACID COMPOSITIONS (wt% as methyl esters) OF PALM OIL AND PALM OLEIN

Type of oil	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0
Palm oil	0	0.23	44.98	0	2.32	43.07	8.80	0.33	0
Palm olein	0.3	1.0	39.80	0.2	4.4	42.40	11.20	0.4	0.4

TABLE 3. TRIGLYCERIDE COMPOSITION BY C-NUMBER (%) OF PALM OLEIN

Triglyceride composition (by C-number, wt. %)	Range	Mean	Standard deviation
C44	0.00-0.30	0.09	0.081
C46	0.40-1.40	0.77	0.266
C48	2.40-3.90	3.28	0.318
C50	37.90-40.90	39.52	0.549
C52	41.90-43.70	42.74	0.435
C54	11.80-13.50	12.80	0.368
C56	0.50-1.00	0.67	0.113

Pure palm olein and five palm olein-based base fluid blends (namely, FG Base 1, FG Base 2, FG Base 3, FG Base 4, FG Base 5), incorporating different quantities of POME as a lubricant auxiliary, were produced in this study, and their lubricating properties were analysed (*Table 4*). A lubricant auxiliary is a chemical constituent or, to be specific, an ester, that poses a high degree of polarity (Repo, 2004). The backbone of the triglyceride molecules of palm olein has different polarities in nature depends on the bound fatty acids. Some forms of polarity exist - enable the linkage or coordination of the polar esters through several different forces

TABLE 4. CHARACTERISTICS OF BASE FLUID BLENDS

Performance characteristic	Pure olein[a]	FG Base 1[b]	FG Base 2[c]	FG Base 3[d]	FG Base 4[e]	FG Base 5[f]	Desired*
NSF registration number (NSF website)	136 685	NA	136 686	136 687	136 88	136 689	-
Specific gravity @ 15°C ($g\ cm^{-3}$)	0.8975	0.8966	0.8946	0.8909	0.8867	0.8817	< 1.0
Viscosity, kinematic @40°C, cSt, ASTM D445	41.66	39.99	32.29	25.56	19.93	15.97	-
Viscosity, kinematic @100°C, cSt, ASTM D445	8.47	7.83	7.17	6.12	5.18	4.41	- -
Viscosity index, ASTM D2270	186	171	196	202	211	206	-
Rotating bomb oxidative stability (RPVOT), (min), ASTM D2272	14	14	14	14	14	14	> 100
Moisture content (%), ASTM D1744	0.085	0.085	0.084	0.097	0.081	0.087	Max. 1%
Air release (min), ASTM D3427	1.90	1.40	1.30	1.60	1.60	1.80	7-10
Demulsibility, oil/water/ emulsion (ml), (min), ASTM D1401	40/35/5, 60	39/36/5, 60	40/38/2, 60	40/40/0, 5	40/40/0, 5	40/40/0, 5	40-40-0, 20
Foam (ml), Seq. I/II/III, ASTM D892	20-0/0-0/290-0	10-0/0-0/70-0	0-0/10-0/20-0	0-0/0-0/0-0	0-0/0-0/0-0	0-0/0-0/0-0	0-0/10-0/0-0
Rust, ASTM D665-A	Pass	Fail	Fail	Fail	Fail	Fail	Pass
Copper strip corrosion, ASTM D130	1a	1a	1a	1a	1a	1a	Max. 2
4 ball EP test, 40 kg/60 kg (mm), IP 239	0.32/1.45	0.33/0.42	0.34/0.40	0.38/1.73	0.40/1.82	0.42/1.96	< 0.5
80 kg/100 kg (mm), IP 239	1.91/2.09	2.08/2.13	1.70/2.21	1.82/2.14	1.95/2.29	2.08/2.35	-

Note: [a] No palm oil methyl esters (POME), [b] 1% POME, [c] 10% POME, [d] 20% POME, [e] 30% POME, [f] 40% POME.
*Desired results are only indicative of more or less acceptable performance according to API, SAE and ASTM standards for biodegradable lubricants, and conform to ISO standards for triglyceride-based fluids.

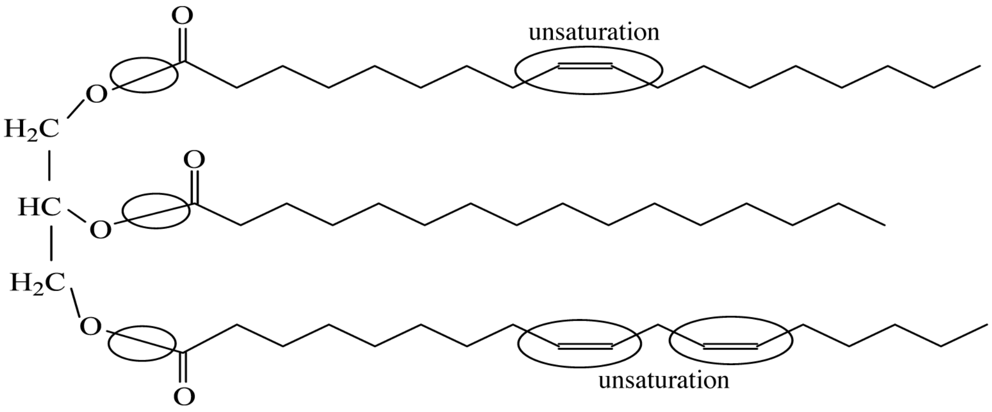

Figure 1. Structure of a triglyceride molecule of palm olein and its reactive sites. Left: glycerol; right, from top to bottom: oleic acid C18:1, palmitic acid C16:0 and linoleic acid C18:2.

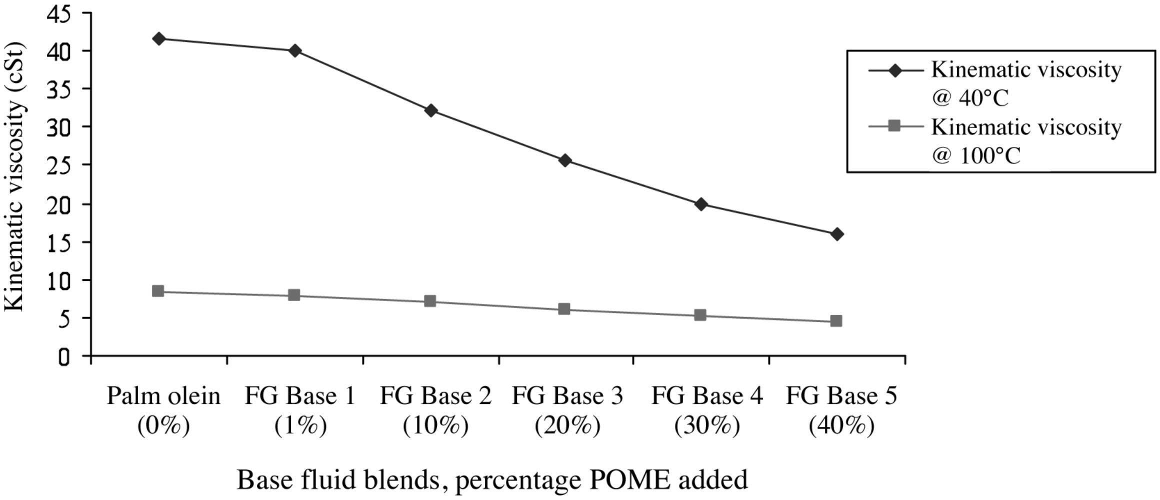

Figure 2. Influence of palm oil methyl esters (POME) on the kinematic viscosity of palm olein.

(*Figure 1*), thus resulting in varying changes in the lubricating characteristics of palm olein (further discussion follows in a later part of this section). It was hoped that POME, being a polar substance, can be used as a lubricant auxiliary to enhance the properties of palm olein as lubricating oil.

Effect of POME on the Lubricating Properties of Palm Olein Base Fluid Blends

Kinematic viscosity. The addition of POME to palm olein indirectly influenced the kinematic viscosities of the base fluid blends. More importantly, the use of POME was able to modify the kinematic viscosities of the base fluid blends to meet the viscosity ranges classified by ISO viscosity grades (ISO VG) for commercial lubricants, having viscosities varying from ISO VG 15 to ISO VG 42. ISO VG is classified based on the ISO Viscosity Classification System (ISO 3448) via the measurement of viscosity (cSt) at 40°C according to ASTM D445. The higher the concentration of POME, the lower was the kinematic viscosity of the base fluid blends (*Figure 2*) due to the relatively low viscosity of POME (4.5 cSt at 40ºC). On the other hand, POME being less viscous than palm olein was unable to improve the tackiness of the base fluid blends; thus, the use of POME was only applicable to the formulation of palm-based lubricants with low and moderate kinematic viscosities. Their viscosity indices (171 - 211) (*Table 4*) were much higher than those of their petroleum counterparts (90 - 150); in fact, the indices were far beyond the desired acceptable value of 100 set by SAE for petroleum-based products, including lubricating oils. Hence, palm-based fluids will not vary much in viscosity over a wide temperature range, and therefore will perform well throughout, thus maintaining their good viscosity ranges and accessibility to all moving parts.

Rust prevention. POME has a high degree of polarity due to its carbonyl bond having two electron lone pairs, which will make it behave as a hydrogen bond acceptor (*Figure 3*). The strong dipole moment

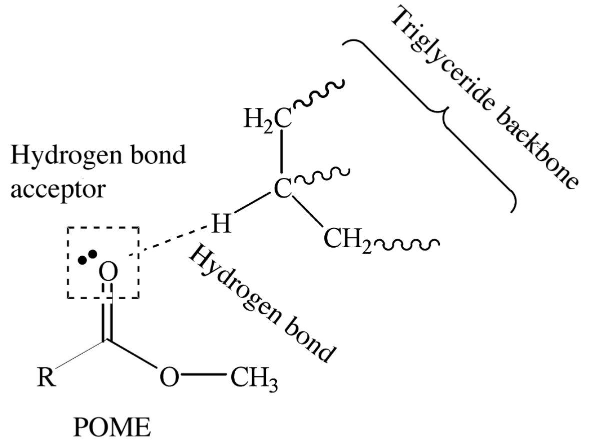

Figure 3. Proposed hydrogen bonding between palm oil methyl esters (POME) and palm olein triglyceride (R denotes any fatty acyl chain present in palm oil).

of the carbonyl functionality induces hydrogen bonding (or van der Waals forces) and ester linkage, binding the triglyceride molecules of the base fluid together. This unique characteristic of the lubricant auxiliary provides and maintains a thin film over the metal parts of machines and the oil contact surface, to smoothen and lubricate these parts. The superior lubricity property provided by POME, however, can compete with the triglyceride molecules of palm olein which have an inherent rust protection property (*Table 4*). The thin film provided by POME tends to form a stronger bond with ferrous metal surfaces than the triglyceride molecules, which stops the triglyceride molecules from covering the surfaces and hence, rendering the surfaces more vulnerable to water (and oxygen) attack. As a result, the protection of the metal surface from oxidation is reduced and eventually leads to the rusting of the metal surfaces. This phenomenon can be observed in the base fluid blends containing POME that had failed the rust tests.

In order to prevent the rust problem arising from the use of POME as the lubricant auxiliary, the incorporation of an anti-wear additive having higher polarity than POME in the base fluid blends becomes necessary. Although POME will naturally compete with the anti-wear additive to cover the metal surface, the latter has a higher affinity (Randles, 1993) for the metal surface, and hence, provides more efficient rust protection and wear prevention, *i.e.* friction as well as wear and tear reduction.

Extreme pressure via 4 ball test. All the base fluid blends including the pure palm olein were found to exhibit moderate 4 ball anti-wear characteristics. The presence of POME at levels ≥ 20% in the base fluid blends was found to promote higher wear characteristics in the 4 ball test compared with the base fluid blends having 1% and 10% POME which inhibited wear (*Figure 4*). This finding corresponds to a previous finding (Randles, 1993) which stated that a polar base fluid (esters) can compete with other less polar constituents in the base fluid to cover the metal surfaces, resulting in higher wear characteristics. In contrast, it was reported elsewhere (Larson and Larson, 2005) that 5% of POME in a mineral oil-based lubricant was appropriate in slowing down the oxidative degradation of the lubricant, reducing wear and corrosion, and improving wear characteristics, but that 10% POME caused more severe oil degradation. In this regard, it is interesting to note that in the present study, 10% POME seemed to react in a different manner and showed improved anti-wear characteristics in the base fluid blends derived from palm olein, whereas other levels of POME showed similar results. While the 5% addition of POME showed improved anti-wear characteristics, the addition of more than 10% POME showed higher wear, most probably due to the reduced viscosity

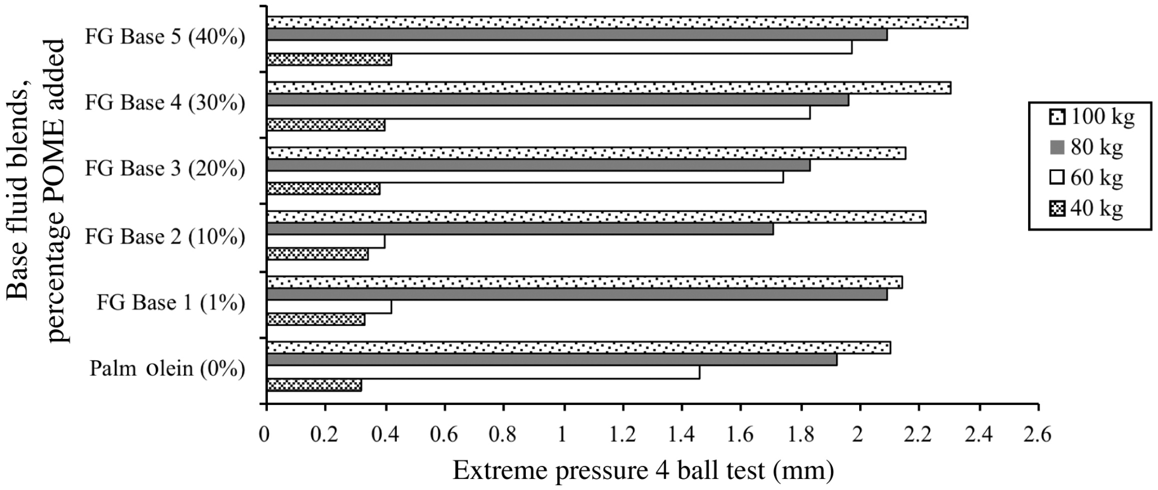

Figure 4. Influence of palm oil methyl esters (POME) on the extreme pressure 4 ball test on palm olein.

exhibited when more POME was added. This will promote rust, encourage friction and wear, making the contact load experience greater scuffing failure, and resulting in greater material loss and energy losses. In short, all the base fluid blends including the pure palm olein exhibited only light to medium load-carrying ability.

Oxidative stability. Adding POME did not seem to reduce oxidation degradation as was claimed elsewhere (Maleque and Masjuki, 2000). There seemed to be no improvement in the oxidative stability of the base fluid blends measured by the rotating pressure vessel oxidation test (RPVOT). In fact, addition of different levels of POME was insignificant in changing the oxidative stability of palm olein. However, the oxidative stability performance test of these base fluids evaluated by the Rancimat test (*Figure 5*) illustrated that there were changes in the Rancimat induction period (IP), with a trend of decreasing IP with an increase in the level of POME. This phenomenon corresponds well with the finding by Larson and Larson (2005), showing that the use of more than 10% POME caused more severe oil degradation than with its petroleum-based counterpart. As POME has typically a lower Rancimat IP (21.8-23.3 hr) than palm olein (22.6-28.0 hr), the substitution of palm olein with POME caused non-linear IP drops in the resulting base fluid blends. In addition to this, the low RPVOT IP (14 min) of the base fluid blends was to be expected due to the presence of significant amounts of the unsaturated fatty acyl chain in palm olein. This unsaturation causes palm olein to be more susceptible to oxidation, and thus more vulnerable to free radical attack than the petroleum counterpart. Thus, all the base fluid blends had low resistance to ageing caused by thermal degradation, and therefore oil life would decrease with the deposition of degradation products unless they were fortified further with specialty additives.

Despite the drawbacks of a few properties of the base fluid blends discussed in the earlier section, POME improved other lubricating properties of the base fluid blends, such as emulsion inhibition and foam inhibition, compared with pure palm olein. Improvement in these properties is desirable to enable the use of palm olein as the major constituent in a base fluid, as palm olein naturally has poor capability in inhibiting emulsion and foam in the presence of excessive water and air as is typical of machine conditions.

Emulsion inhibition. The base fluid blends, FG Base 1 (1% POME) and FG Base 2 (10% POME), performed poorly in emulsion inhibition, whereas the three other base fluid blends (≥ 20% POME) showed excellent demulsibility property (*Figure 6*). POME with its high polarity ester linkage provides hydrogen bonding, adhering to the metal surfaces and to the oil (triglyceride molecules) contact surface. As a result, the interfacial tension of the two phases (oil and water) increases in the presence of water, which favours the break between the water molecule and the lubricant surface. The decreased mutual adhesion (Hodges, 1996) between the two phases was most effective when POME was present in the base fluid blends at more than 10%. Emulsion was formed in the pure palm olein and in the base fluid blends with less than 10% POME, mainly due to the comparatively

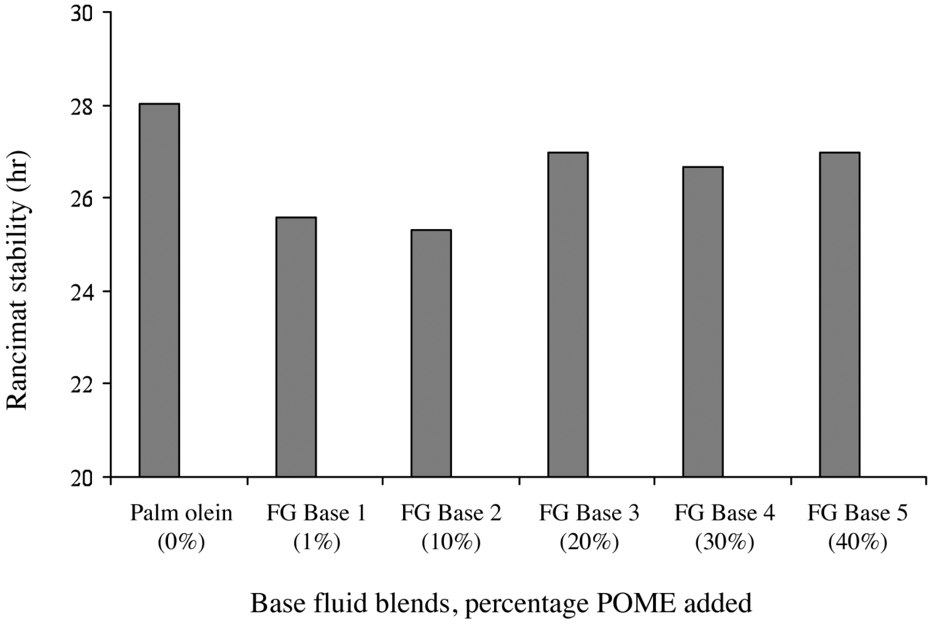

Figure 5. Influence of palm oil methyl esters (POME) on Rancimat stability of palm olein.

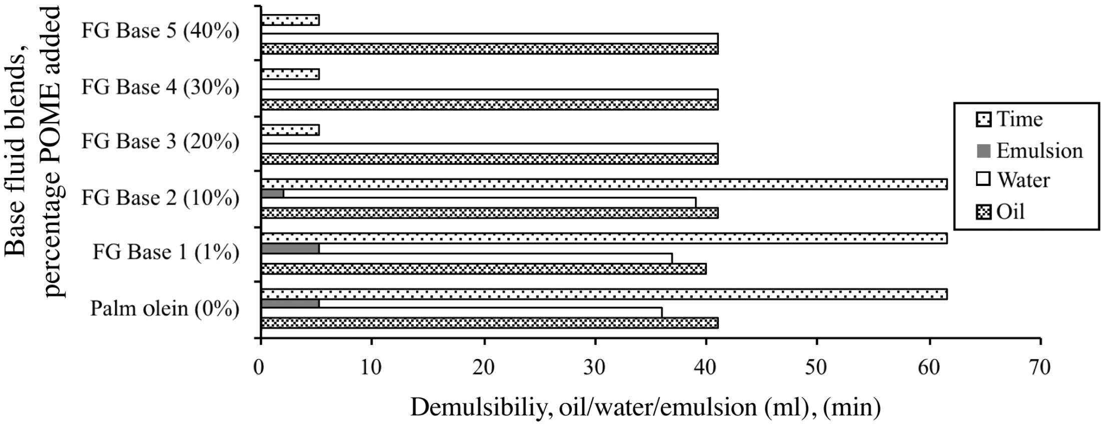

Figure 6. Influence of palm oil methyl esters (POME) on demulsibility of palm olein.

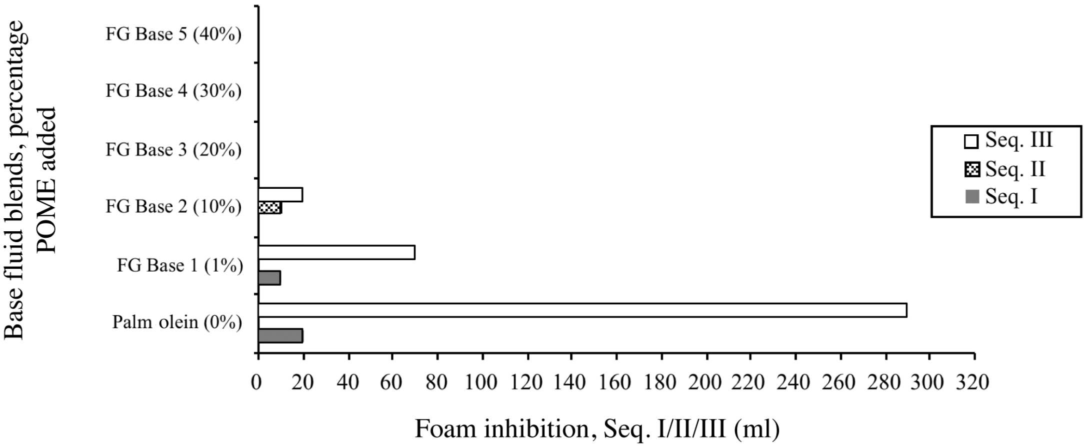

Figure 7. Influence of palm oil methyl esters (POME) on foam inhibition of palm olein.

weaker interfacial tension between the two phases. These base fluid blends contained mainly oil or triglyceride molecules with fatty acyl chains, which have greater affinity to water due to the hydrophobic and hydrophilic nature of the oil. In the absence of sufficient hydrogen bonding from POME, the tendency of the surface of oil molecule to contract is less, compared with that of water having high polarity. The water-loving affinity of fatty acids in the oil lowers the interfacial tension between the oil and water, making them remain in contact for a longer time.

Foam inhibition. Foam inhibition was excellent for all the base fluid blends except for pure palm olein (*Figure 7*). The base fluid blends enriched with POME impacted the rate at which air detrained from the lubricating fluids, as the high polarity characteristic of the esters tended to increase the interfacial tension between the oil bubbles (Maleque *et al*., 2000), causing small bubbles to form into larger units, and subsequently break down the foam (air globules) from the fluid more effectively. Triglyceride-based palm olein has lower interfacial tension with air, and thus has a higher tendency to foam.

Air release and copper corrosion. The presence of POME did not affect the air release (*Figure 8*) and corrosion inhibition (*Table 4*) abilities of all the base fluid blends compared to pure palm olein. All of them had significantly shorter air release time (< 2 min) compared to the desired air release time of 7-10 min which is accepted widely for commercial petroleum products. In addition, they passed the copper strip corrosion test at 100°C for 3 hr. Surprising, palm olein also had inherent air release and corrosion inhibition properties.

Pour point, cloud point and flash point. Originally, POME is used mainly as fuel (biodiesel). It has a high pour point, cloud point and flash point, *i.e.* 12.0°C, 12.6°C and 174°C, respectively. When POME is used as a lubricant auxiliary for blending with palm olein as the lubricant mixture, the respective fuel properties of the base fluid blends were altered, *i.e.* pour point was reduced to 6°C, cloud point ranged from 6.7°C to 8.2°C, and flash point ranged

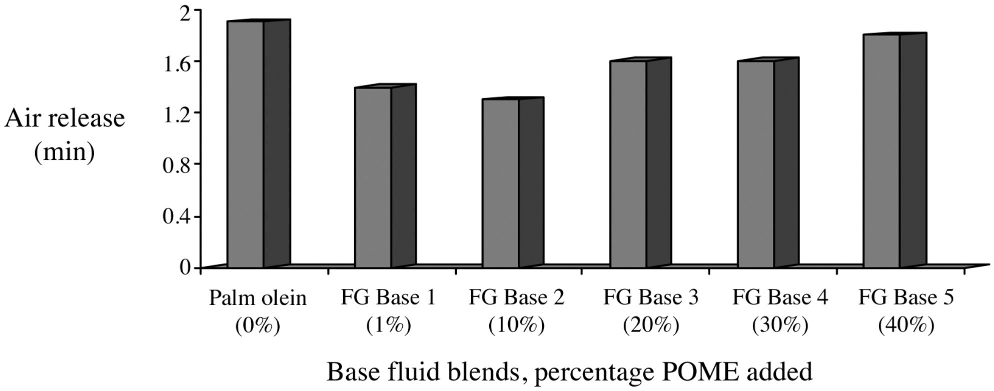

Figure 8. Influence of palm oil methyl esters (POME) on air release property of palm olein.

TABLE 5. CHARACTERISTICS OF COLD FLOW, FLAMMABILITY AND COMBUSTIBILITY OF BASE FLUID BLENDS

Sample code	POME	Pure olein	FG Base 1	FG Base 2	FG Base 3	FG Base 4	FG Base 5
Pour point[a] (°C)	12.0	6.0	6.0	6.0	6.0	6.0	6.0
Cloud point[b] (°C)	12.6	6.6	6.7	7.2	7.6	8.2	7.1
Flash point[c] (°C)	174	305	295	282	276	248	232

Note: [a] ASTM D97.
[b] ASTM D2500.
[c] ASTM D93.

from 232°C-295°C, and were comparable to pure palm olein (at 6°C, 6.6°C and 305°C, respectively) (*Table 5*). Flash point exhibited by all the base fluid blends was far beyond the desired range for petroleum products/lubricants according to SAE specification, *i.e.* more than 200°C. However, the high pour point and cloud point would result in poorer cold flow characteristics, thus limiting their use in temperate countries.

The base fluid blends comprising palm olein and POME auxiliary were previously NSF (National Sanitation Foundation)-certified food-grade HX-1 ingredients for food-grade lubricant H1 formulation with incidental food contact. The products were listed from 2006-2009 in the NSF White Book Listing of Nonfood Compounds (NSF website). They are NSF-certified HX-1 base fluids suitably used to substitute the unsafe and toxic petroleum-based fluids in lubricant formulations for use with incidental food contact in and around food-processing areas. They are inexpensive, readily available, biodegradable, environment-friendly and renewable. Besides reducing the dependency on petroleum, they help protect the global environment from pollution.

CONCLUSION

POME, an identified ester auxiliary with desirable high polarity, was able to enhance some of the lubricating properties of palm olein used as a lubricating oil. POME increased the overall polarity of palm olein-triglyceride molecules, and hence, increased the lubricity of the base fluid blends as indicated by the wear reduction characteristics, when POME was added up to 10%. Beyond this level, the wear characteristic pattern changed drastically. The properties of emulsion and foam inhibition were greatly improved with increasing levels of POME compared with pure palm olein; and the excellent air release and corrosion inhibition properties together with high viscosity index were naturally inherited, independent of the amount of POME added. Although other properties, *e.g.* oxidative stability (RPVOT), rust and load-carrying capability (by 4 ball tests), were inferior in nature and were commonly found in all vegetable oil-based lubricating fluids, there are many different ways (*i.e.* by chemical or genetic modifications to the triglyceride molecules of the oils) to further improve the lubricating properties of these base fluids. The rest of the properties disclosed were of a voluntary nature, depending on the type of base fluids required for use. Base fluids with 5% to 10% addition of POME were the most outstanding in terms of their performance in load-carrying capacity, whereas base fluids with the addition of 20% to 40% POME showed the most significant capability of inhibiting emulsion and foam. In short, the overall lubricating properties for all the base fluid blends fortified with POME were satisfactory, while their shortcomings, *i.e.* rust prevention properties, could be easily overcome with commercially available specialty additives.

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