

BIODEBASED LUBRICANTS
Harnessing the
Richness of Agriculture
Resources



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ABSTRACT

In Malaysia, the availability of diversified biomass feedstocks such as sugars, oils, protein, lignocellulosics, combined with numerous biochemical, thermo and chemical conversion technologies, offers a wealth of products that are useful in many applications. Target applications include polymer, lubricant, solvent, adhesive, herbicide, and pharmaceutical industries. Many of these industrial biobased products have already penetrated the markets, but improved technologies promise new products that can compete with fossil-based products in both cost and performance aspects. Among these markets, the biolubricant market represents an enormous potential for biobased products.

Despite the increased popularity of the biobased or green products, the development of these products is a challenge because the sustainability aspect of these biobased chemicals is still being dispute. The possibility of achieving the environmental sustainability is questioned—considering the environmental degradation, climate change, overconsumption, and the pursuit of economic balance within the closed system. To tackle these issues effectively requires reverting to fundamental principles that govern the technologies that produce these chemicals. Are these technologies efficient and effective? (Developing technology that uses less energy produces less waste, and safer to environment). This is the paradigm shift of the early 21st century; innovating technologies for sustainable development. Ways of reducing negative impacts on human are also paramount which entails environmental-friendly engineering, environmental resources management and environmental protection.

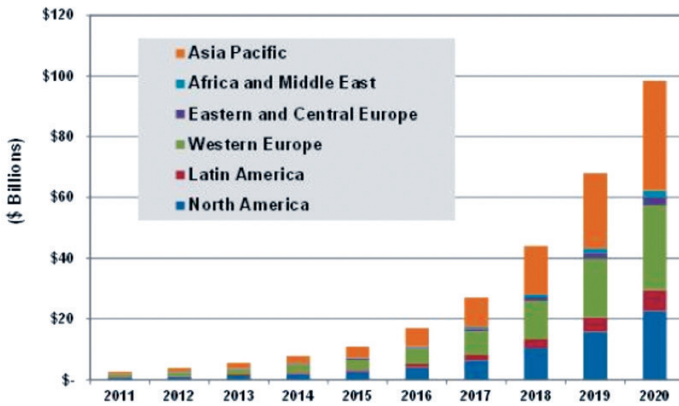
Lubricants which are both readily biodegradable and non-toxic to humans and environments are known as biobased lubricant or biolubricant. A biolubricant can be any plant oil or synthetic esters, which are derived from plant oils. In pursuit of environmentally

friendly chemical engineering, various biolubricants from synthetic esters derived from agriculture resources have been developed using low-pressure technology. The technology enables product synthesis to take place at low temperature and pressure. In addition, the reaction time was markedly reduced and the product conversion was improved. Using the pulsed loop reactor, the methyl ester (biodiesel) can be produced in 10 minutes at 60°C and the polyol ester in 30 minutes. Similar loop reactor under vacuum condition was also used to produce various esters for biolubricants. Hydraulic fluid, metal working fluid, tapping oil, oven chain oil, and drilling fluid are among the biolubricants that are currently being developed for commercial purposes. Changing the starting materials for the synthesis allows us to tailor make the final ester for selected applications. Ester-based oil drilling fluid (or mud) has also been developed to address the increasing concern of the environmental consequences of using oil based mud (OBM) using the low-pressure technology. The ester-based mud is superior to the commercial ester, and the production cost is much lower due to the efficient technology. Incorporating graphene in the ester-based mud has further improved its performance. The ester-based mud enhanced with graphene has potential to be used for high temperature application above 450°F. Green transformer oil is another environmentally friendly product that is developed driven by the desire for a safer, non-flammable and environmentally acceptable insulating liquid for use in power equipment.

INTRODUCTION

Biobased products are commercial or industrial products or intermediate ingredients or feedstocks (other than food or animal feed) that are composed in whole, or in significant part, of biological products, renewable agricultural materials (including plant, animal, and marine materials), or forestry materials (US Farm bill, 2008). Malaysia have abundant of agro-biomass resources such as from palm oil, sugar cane, cassava, coconut, and wood. The rich and diverse biomass resources offer immense opportunities for establishment of a biobased economy in Malaysia. Nevertheless, while demand for biofuels is very much driven by regulation, the demand for biobased chemicals is usually promoted by economic drivers as well as end users' interest for green products. The market value for biobased or green chemicals by regions is shown in Figure 1.

Green Chemical Market Value by Region, World Markets: 2011-2020



(Source: Pike Research)

Figure 1 Green market value by region, world market: 2011-2020

Biolubricants derived from vegetable oils are biodegradable, and have low ecotoxicity as compared to mineral oil-based lubricants. However, several studies showed evidence of the limitation of vegetable oils as lubricants without structural modification. In Malaysia, due to the availability of palm oil, the raw material used in the production of synthetic biolubricant is mostly from palm oil. Malaysia's palm oil industry accounts for more than five per cent of the country's annual exports. The push to move into this higher-value segment of the palm industry is one of the major initiatives under Palm Oil NKEA. EPP 6 of this NKEA focuses on developing high value oleo derivatives and bio-based chemicals. (<http://etp.pemandu.gov.my/>). However, in 2013, only 18.6 per cent of Malaysian palm oil exports were made up of downstream products, compared to the 81.4 per cent of exports comprising upstream products. Therefore, it is imperative for Malaysian companies to invest further resources in downstream segments or in research and development (R&D) to ensure the industry's long-term sustainability. Since the start of this EPP 6, seven companies have committed investments totaling RM1.35 billion to produce these high-value oleo derivatives and biobased chemicals .

Biolubricants are both readily biodegradable and non-toxic to both humans and aquatic environments. 95% of the biolubricant comprises of its base oil. Biolubricant has been identified as one of the key products in oleochemicals value chain. The market for it has expanded gradually since 2010 due to the increased awareness on the harmful effect of mineral oil-based lubricants to human beings and environment (Thinnes, 2011). Emery Oleochemicals Group, for example, plan to will invest RM416.2 million in three sub-projects to develop and produce palm oil-based bio-lubricant and green polymer additive as well as surfactants for home and personal wellness products.

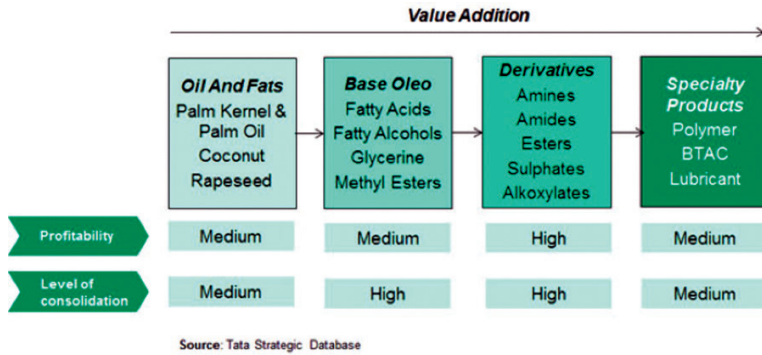
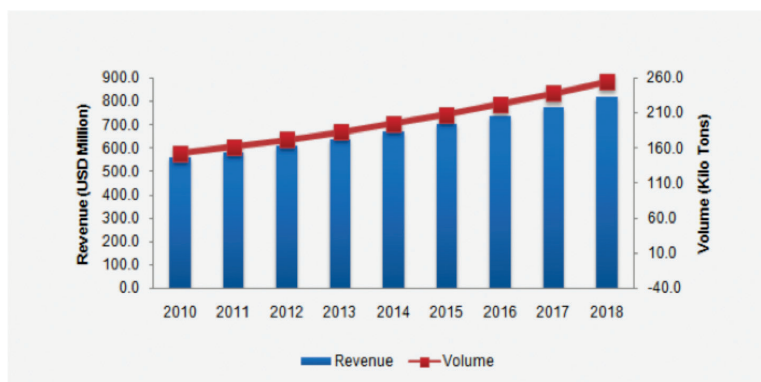


Figure 2 Opportunity in oleochemicals value chain

Our journey in the development of biobased lubricants began about a decade ago. A low-pressure technology was discovered which manipulated the thermodynamics of the process enabling the reaction to be completed in minutes. The conventional method to produce a biobased synthetic ester or biolubricant was via a reaction route involving polyol and fatty acids. In our approach, the methyl ester was used instead of fatty acids to produce the synthetic ester. The use of methyl ester as starting material allowed for the process to be conducted under low pressure and low temperature conditions. This technology uses less energy, produces less waste, and is safer to the environment. In addition, the ester-based biolubricants are harmless to human and environment thus responds to the challenge for sustainable development.

Biobased Lubricants: Harnessing the Richness of Agriculture Resources



Source: ICIS, United Soybean Board (USB), IENICA, Primary Interviews, Transparency Market Research

Figure 3 Europe bio-based lubricants market volumes and revenues, 2010-2018 (kilo tons) (USD million)

Table 1 World lubricant demand projected from 2005-2015

World lubricant demand (thousand metric tons) Item	2005			% Annual growth	
	2005	2010	2015	2005-2010	2010-2015
World lubricant demand	36,250	36,700	41,650	0.2	2.6
North America	10,800	8,820	9,300	-4.0	1.1
Western Europe	5,250	4,800	5,000	-1.8	0.8
Asia-Pacific	11,570	13,530	16,500	3.2	4.0
Other regions	8,630	9,550	10,850	2.0	2.6

While most of the biobased products in Malaysia are derived from agriculture waste/biomass from palm oil industry such as empty fruit bunches, oil palm fronts and palm oil mill effluents, the technology to produce biobased chemicals from lignocellulosic biomass faces additional hurdles. Biobased chemicals derived from ethanol can only be produced on a commercial scale once the process of converting lignocellulosic biomass to ethanol has been optimized. However, the production of other (non-ethanol) biobased chemicals from lignocellulosic biomass is even more difficult

(Felda Global, 2014). Consequently, methyl ester, which can be produced either from waste cooking oil or byproducts from vitamin E plant, is chosen in the low-pressure technology to produce these high-value oleo derivatives. The fact that methyl ester has higher vapor pressure than fatty acids. It improves the separation of the final product from the unreacted components thus enhanced product purity. Methyl ester is derived from palm oil, the biodegradability and green attributes sought for in most lubricants are intrinsic in the palm oil-based lubricants.

Based on years of research dedicated to the development of different types of biobased synthetic esters for biolubricant applications, our research team has developed and patented various products and technologies. The most outstanding discovery was filed in 2003 and patented in 2010 (MY 14333A). It is on the synthesis of trimethylolpropane (TMP) esters from palm oil and palm kernel methyl esters using low-pressure technology. The new palm oil-based TMP esters are alternative base oils for lubricant manufacturers. Since the starting ester is derived from palm oil, the biodegradability and ecotoxicological attributes sought for in most lubricants are intrinsic in the low-pressure lubricants. Moreover, the problem with the pour point (PP) associated with the level of saturation in palm oil was resolved, as the PP of palm oil-based TMP ester was successfully lowered to -36°C . With proper additives such as antioxidants, the formulated palm oil-based TMP esters offer a wide range of applications: hydraulic fluids, fire resistant hydraulic oils, metalworking fluids, and general lubricating oils. Since then, various biobased synthetic esters with different properties have been developed for applications such as food-grade lubricant (Aziz *et al.*, 2014), drilling fluid (Abdul Habib *et al.*, 2014), engine oil (Zulkifli, *et al.*, 2014), metal working fluid (Chang *et al.*, 2013), hydraulic fluid (Alias *et al.*, 2009). This report highlights some of

the findings from our synthesis and formulation work. In addition, development work in methyl ester synthesis is also included since the ester is used as the starting raw material in all our researches.

METHYL ESTER

Introduction

Methyl ester or commonly known as biodiesel has attracted attention from various parties such as researchers, politicians, businessmen and social workers due to its potential as a valuable substitute to diesel fuel and also for its environmental benefits (Wilson, 1980). The environmental issues particularly on the growing carbon dioxide emissions, global warming, and declining of petroleum fuels reserves escalate the interests. Conventionally, methyl ester can be produced from plant oils, animal fats and waste cooking oils. The non-edible plant oils are mostly selected as the feedstock of methyl ester for biodiesel compared to edible oils because of the food security issues. The non-edible oils mostly contain toxic components which can cause vomiting, dizziness, and sometimes fatality. Therefore, they cannot be used for human being consumption. Besides, the biodiesel manufacturers can also use waste cooking oil to produce methyl ester.

Currently, many reports on biodiesel production describe synthesis methods conducted under batch mode using various types of reactor configurations, such as plug flow reactors, batch reactors, fixed bed reactors and stirred tank reactors. Harvey et al. (2003) reported that the long residence times of batch processes led to problems such as high capital costs and the need for complex control systems. Recently, continuous pulsed loop reactors and oscillatory flow reactors (OFR) have been tested for biodiesel production. A pulsed loop reactor is a tubular reactor in which orifice plate baffles

are equally spaced and a pulsed flow is produced using a piston drive. This type of reactor is normally used in the fields of heat and mass transfer, residence time distributions, size distributions, flow patterns and mixing studies (Palma and Giudici, 2003; Reis *et al.*, 2004). The oscillatory flow reactor allows these processes to proceed in a continuous manner, thereby intensifying the process and improving the economics (Harvey *et al.*, 2003).

Transesterification of Vegetable Oil using Oscillatory Flow Reactor

A 3.5 litre oscillatory flow reactor was designed and fabricated to synthesize methyl ester from various feedstock materials. (Sham *et al.*, 2012). This is because the free fatty acid content of many feedstocks is normally above 10%, the oil must be pre-treated prior to the transesterification process. In this study, the synthesis of methyl ester (ME) using methanol (MeOH) was carried out using two alkaline catalysts: potassium hydroxide (KOH) and sodium hydroxide (NaOH). The operating parameters that affected the transesterification reaction in the pulsed loop reactor were the frequency of oscillation, the ratio of MeOH to oil, the amount of catalyst, the reaction temperature, the reaction time, and the free fatty acid content of the feedstock. Thus, the aim was to determine the optimum values of these operating conditions. The physical and chemical properties of the biodiesel were also analysed and compared to the characteristics of fossil-based diesel fuel.

As the mixing process in this reactor was achieved through the superimposed oscillatory motion, the frequency of the piston movement played an important role in speeding up the rate of reaction. The oscillatory motion facilitates excellent mass transfer and energy transfer once the reactants have reached the baffles under the superimposed flow condition. As shown in Figure 4, there is

a direct correlation between the biodiesel yield and the oscillation frequency, which is represented by the oscillatory Reynolds number (Reo) (Sham *et al*, 2012). The nature of the oscillatory flow depends significantly on the oscillatory Reynolds number, particularly the frequency of oscillation. The rate of mass transfer is accelerated by decreasing the surface tension of the liquid due to thermodynamic effects. Below 6 Hz (Reo between 1400 and 1700), the yield of biodiesel was very low. Under these oscillation frequencies, fluid mixing decreased due to fewer numbers of flow vortices, which resulted in a lower mass transfer rate. However, at oscillation frequencies above 6 Hz (Reo >2100), no significant increase in biodiesel yield was recorded. Beyond the reaction equilibrium (6 Hz), the maximum reaction conversion will not be affected unless a new equilibrium position is attained.

The molar ratio of the excess reactant to the limiting reactant is one of the most important variables affecting the percent conversion to ME. In this reaction, MeOH was the excess reactant and oil was the limiting reactant. A large excess of alcohol is usually required to drive the reaction to the product side. The maximum molar ratio employed in this experimental work was 7:1.

Based on the reaction stoichiometry, 99% conversion of oil (2000 g or 2.30 moles) will result in the production of 6.9 moles of ME. The maximum reaction yield was achieved at a molar ratio of 6:1, as shown in Figure 4. As seen in the graph, a lower conversion was observed at lower molar ratios since the percent conversion of triglyceride was less than 98%. This observation indicates that a higher molar ratio of MeOH to oil results in better transesterification reaction.

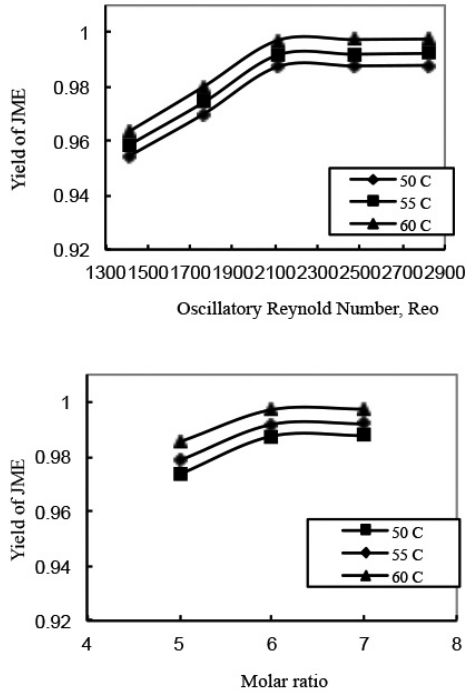


Figure 4 Effect oscillation Reynolds number and molar ratio at various temperatures (Sham *et al*, 2012)

The importance of the excess MeOH in the transesterification process has been reported often in the literature because MeOH drives the forward reaction and is the key to ensuring the formation of the desired methyl ester product. Additionally, it promotes the dissociation of intermediate compounds once the initial complex is formed (Oommen, 2002). Figure 4 also indicates that at a higher ratio (7:1), the results did not show any improvement in terms of reaction yield. The maximum conversion to methyl ester occurred at 6:1 molar ratio and 6.0°C

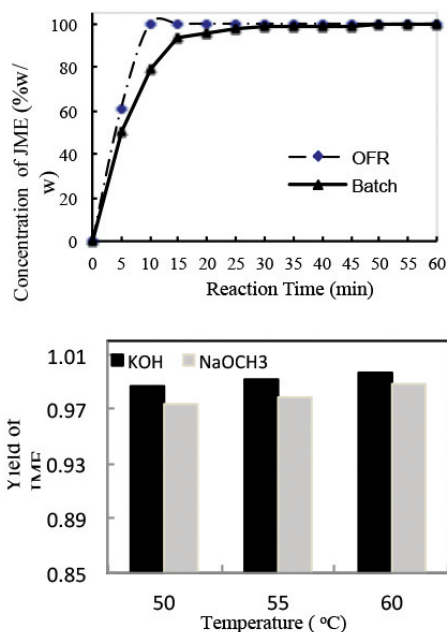


Figure 5 Effect of reaction time and catalyst at various temperatures

The rate of the transesterification reaction also depends on the time of reaction, as shown in Figure 5. The reaction at 60°C accelerated after 10 min of the reaction. The reaction only took 10 mins to reach the maximum conversion as compared to 30 min required by the batch reactor. Similar work using an oscillatory flow reactor for the transesterification of vegetable oil using hydroxide catalyst revealed a longer reaction time of 30 min to reach about 90% conversion to methyl ester (Harvey *et al.*, 2003). This result shows the advantage of using oscillatory flow reactors over batch reactors; the reaction time can be reduced by 50%. As mentioned earlier, the oscillatory mixing induced by the piston promoted mass transfer between the liquids, which further accelerated the rate of reaction.

Previous studies on transesterification of vegetable oils and animal fats suggested that the conversion of vegetable oil into methyl ester may be affected by the catalyst loading. Based on an earlier study using a batch reactor, the optimum percentage of catalyst was found to be 1% w/w, and this amount was used for all experiments (Rouse, 1998). The effects of different types of catalyst on product yield in OFR were investigated using potassium hydroxide (KOH) and sodium hydroxide (NaOH). Based on Figure 5, it can be observed that the yield of ME increased steadily with temperature, for both KOH and NaOH catalysts. For an endothermic reaction, higher temperature results in higher conversion to the methyl ester product, as shown above. This finding is supported by a kinetics study on transesterification that showed the dependency of the rate constants on the reaction temperature (Plessner and Reynolds, 1976). However, the yield of methyl ester was always higher for the KOH catalyst and for the NaOH. The highest yield of methyl ester was achieved at 60°C using KOH catalyst. In addition, it was observed that using NaOH catalyst produced substantial amount of soap/gel materials that will consequently reduce the yield of methyl ester. The catalyst forms alkaline soaps with fatty acids, thus reduces the catalyst efficiency and increases the oil viscosity (Oommen, 2002).

Properties of Methyl Ester

To meet the requirement of methyl ester specifications, the analysis of the physical and chemical properties of the methyl ester was performed to compare against the standard biodiesel specifications. The selected physical and chemical properties include kinematic viscosity, density, acid number, pour point, cloud point, water content, carbon residue, iodine value, calorific value and flash point. These analyses followed an acceptable certified standards

method, such as the ASTM methods. Table 2 shows the properties of *Jatropha curcas* methyl ester and the comparison to diesel fuel characteristics. In this study, the results show that the heating value of *Jatropha curcas* methyl ester is comparable to that of the diesel. In addition, the carbon residue is lower and the flash point is higher than the diesel fuel. Even though the kinematic viscosity of *Jatropha curcas* methyl ester is very much higher than that of the diesel fuel, the pour and cloud points are still comparable.

Table 2 Physical and chemical properties of methyl ester and comparison with diesel fuel characteristics

Properties	<i>Jatropha curcas</i> methyl ester	Diesel*
Kinematics viscosity (mm ² /s)	4.33	2.6
Density (Kg/m ³)	866	850
Acid number (mg KOH/g oil)	0.738	-
Pour point (°C)	-10	-15
Cloud point (°C)	-6	-10
Water content (%)	0.004	0.02
Carbon residue (% mass)	0.03	0.17
Iodine value (g iodine/100 g)	99	94
Calorific value (MJ/Kg)	38.72	42
Flash point (°C)	73	68

*(tapannes,2008]

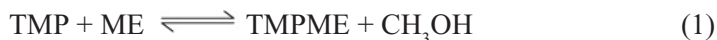
BIOLUBRICANTS FROM TRIMETHYLOLPROPANE ESTERS

Synthesis of Palm Oil-based Trimethylolpropane Ester

Biolubricants derived from vegetable oils are renewable and completely biodegradable, and have low ecotoxicity as compared to mineral oil-based lubricants (Schneider, 2006). Nonetheless there are some performance limitations associated with them, e.g. thermal, oxidative, and hydrolytic stability; and inadequate low temperature fluidity due to high pour point (Wilson, 1998). These limitations can be minimized by means of chemical modification through transesterification of vegetable oils with polyhydric alcohols or polyols (Sharma *et al.*, 2006). This process causes the elimination of hydrogen atom from the-carbon of the vegetable oil structure and provides ester with high degree of oxidative and thermal stability which is seldom found in vegetable oils (Wagner *et al.*, 2001). Several studies have evidenced the improvement in performance of vegetable oils through their structural modification (Hwang *et al.*, 2001; Hwang *et al.*, 2003; Sulaiman *et al.*, 2007; Lathi and Mattiasson, 2007; Sharma *et al.*, 2008; Campanella *et al.*, 2010).

Trimethylolpropane triester (TMPTE) has been synthesized as base oil for various types of lubricating oils by using TMP and vegetable oil methyl ester as starting materials (Yunus *et al.*, 2002; Yunus *et al.*, 2003a,b; Yunus *et al.*, 2004; Yunus *et al.*, 2005). In Malaysia, palm oil-based methyl esters (PME) are assuming an increasingly important role as starting materials in the oleochemical industry. Methyl esters are reportedly superior to fatty acids (FA) for producing a number of FA derivatives. Their production cost is also more competitive owing to lower capital and energy costs. Consequently, PME are chosen as starting materials in the

synthesis of TMPTE as lubricant base oil. The transesterification reaction involves cleavage of an ester group, RCOO–, from PME by the –OH group of TMP to produce the new palm oil-based TMP esters. Since there are three –OH groups in TMP, the process yields intermediate formation of monoesters (TMPME), diesters (TMPDE), and triesters (TMPTE). Methanol (M = CH₃OH) is a by-product that is removed to ensure completion of the reaction. The reaction scheme is shown below:



The overall reaction is as follows:



Scheme 1

A complete conversion of trimethylolpropane (TMP) to palm based TMP ester was obtained under a reduced pressure of 10 mbar in 15 minutes (T=120-130°C, 3.9:1 ratio) using sodium methoxide as catalyst. The intermediate esters namely, monoesters (TMPME) and diesters (TMPDE) were subsequently converted into triesters (TMPTE) in another 30 minutes. The overall reaction reached the completion in approximately an hour, a period far less than reported earlier on rapeseed oil methyl ester of 10 hours (Uosukainen, 1998). The improvement of the current work is attributed to efficient vacuum and higher excess of methyl ester used in the reaction. Palm based TMP esters containing 98% w/w TMPTE was successfully synthesized in this work. The optimum condition was established at 120°C and 20 mbar. While lower reaction temperature and duration

of completion was reported at a much higher ratio, but economically it will not be viable for industrial application.

The vacuum system purges the methanol away from the system, hence creating an environment which favors the forward reaction. In addition, the use of high percentage excess PME has suppressed the backward/reverse reaction further. In fact, using the ratio of PME: TMP at 10:1 reduced the reaction time from 45 at 3.9:1 to 20 minutes. The optimum reaction temperature at 10:1 was notably lower i.e. 80°C as compared to 130°C at 3.9:1 (Yunus *et al.*, 2002). The effect of temperature on palm oil methyl ester transesterification with TMP is shown in Table 3. Initially, the yield of TMPTE increased with temperature but dropped slightly at temperatures above 120°C. Although, the yield of triesters at 130°C was lower than at 120°C, the amount of TMPDE at 120°C was notably higher. When the amount of PME in the reactor is low, the occurrence of reverse reaction could not be suppressed. Consequently, there was a high concentration of diester, TMPDE (12.7 % w/w) in product composition as shown in Table 3.

Table 3 Effect of temperature on palm oil trimethylolpropane ester synthesis (Yunus *et al.*, 2002)

T (°C)	100	120	120	130	140
PME	25.4	25.3	11.2	24.3	23.7
TMPME	0.2	0.4	0.6	0	0.0
TMPDE	7.0	6.1	12.7	1.3	5.3
TMPTE	67.4	68.2	76.1	74.4	71.0

Application of vacuum is vital in the transesterification of palm oil-based methyl esters with TMP. Forward reaction shown in Scheme 1 is favored by either continuous removal of methanol or use of excess methyl esters. Removal of methanol is achieved by either

vacuum or high temperature process. In the absence of vacuum, an operating temperature of at least 200°C is required to produce a reasonable conversion to polyol esters (Basu *et al.*, 1994; Eychenne *et al.*, 1998). The effect of vacuum on the rate of transesterification between PME and TMP at 130°C is shown in Table 4. The analysis of the reaction products was done using the gas chromatography (GC) technique as described by Yunus *et al.* (2002). Although the highest yield of TMPTE was obtained at 0.1 mbar, considerable energy would be needed to achieve this high vacuum condition. The composition of TMPTE at 0.1 and 10 mbar were 82.6% and 79.9% w/w respectively. At 50 mbar, the product contained 75% TMPTE, 1-% TMPDE and 24% of excess PME. While at 10 mbar, the product consisted of 79.9% TMPTE, 2.8% TMPDE and 17.3% of excess PME. Since the difference is marginal, it is anticipated that vacuum pressure between 10-50 mbar, would be sufficient for palm oil TMP ester synthesis. Although the amount of unreacted PME would be high at this condition, it is eventually removed by distillation (Yunus *et al.*, 2002, Yunus *et al.*, 2003b).

Table 4 Effect of vacuum on palm oil trimethylolpropane ester synthesis at 130°C (Yunus *et al.*, 2002)

P (mbar)	500	100	50	10	0.1
PME	41.6	30.7	24	17.3	23.9
TMPME	4	0.6	0.2	0	1.5
TMPDE	27	13.5	1	2.8	8.5
TMPTE	26.4	55.3	74.8	79.9	66.1

The results from this study also indicated that the effect of methyl esters to TMP ratio had little influence on the reaction conversion. However, the optimum molar ratio was established

at 3.8:1. The amount of catalyst required for transesterification of palm oil-based methyl esters and TMP also showed marginal effect but the optimum was proposed at 1.0% w/w. A quantity which is far less than required in biocatalyst using lipase, 40-50% (w/w). Nevertheless, more investigation is still necessary since the effects of all the intermediate esters on the base oil properties have not been yet clearly clarified. The kinetics of transesterification of palm oil-based methyl esters with trimethylolpropane was also conducted which highlighted the complexity of the transesterification reaction (Yunus *et al.*, 2004a). The properties of TMP ester base oil is shown in Table 5 (Yunus *et al.*, 2004b).

The pour point of palm oil-based TMP lubricant is usually above 5°C due to the saturated fraction of fatty acid ester in palm oil. However, to produce the lubricant with low pour point requires the use of high oleic methyl ester as the starting material. Yunus *et al.*, 2005 reports the synthesis of palm oil based trimethylolpropane esters with improved pour points using high oleic methyl ester. In addition, it was also discovered that using alkaline catalyst promotes soap formation, which reduces the yield of esters. Thus, further study is required to find ways to reduce soap formation in the TMP ester synthesis. The presence of double bond in the TMP ester also affects its oxidative stability. Epoxidation of the double has been investigated and presented in the subsequent section (Naidir *et al.*, 2012, Naidir *et al.*, 2011).

Table 5 Chemical and corrosion properties of palm oil-based lubricants (Yunus *et al.*, 2002)

	Method	POTE 1	POTE 2	LZ 1	AG310
Total Acid number	ASTM D-664	0.10	0.35	2.46	0.05
Total Base number	ASTM D-2896	0.42	0.35	0.73	0.15
Density @ 15°C	ASTM D-4052	0.9172	0.9195	0.9196	0.9204
Hydroxyl Value	ASTM D-664	4.5	17.6	7.3	3.7
Iodine Value	AOCS Cd 1c-85	85.9	73.5	82.6	89.6
Saponification Value	AOCS Cd 3a-94	188.9	185.6	196.1	199.9
Color	ASTM D-1500	1.0	1.0	1.0	1.0
Noack (%) Volatility	ASTM D-5800	1.4	2.4	1.5	0.4
Flash Point	ASTM D-92	340	330	310	322
Copper Corrosion	ASTM D-130	1a	1a	1a	1b

Effect of Catalyst on Soap Formation

Catalyst generally plays a crucial role in the production of TMPTE for obtaining better yield in less time. Uosukainen *et al.* (1998) achieved 99% conversion to triester in 10 hr. while using homogeneous sodium methoxide, 64% in 24 hr. with *Candida rugosa* lipase, and 90% in 66 hr. by employing immobilized *Rhizomucor miehei* for production of TMPTE from rapeseed oil methyl ester.

Moreover, Gryglewicz *et al.* (2003) obtained a yield of 85%–90% after a reaction time of 20 hr. for the transesterification of TMP with methyl ester of animal fat in the presence of calcium methoxide as heterogeneous catalyst. These studies reveal inadequate performance of enzymatic catalysts for polyol ester production. Homogeneous catalysts showed good reaction activity by reducing the mass transfer resistance but they had suffered serious drawbacks in terms of saponification and product purification.

Yunus *et al.* (2003) conducted the transesterification of TMP with PME in a batch reactor utilizing sodium methoxide as homogeneous catalyst and successfully to obtain trimethylolpropane ester containing 98% w/w triester in less than one hour. However, the presence of alkali metal catalyst contributed to saponification due to the formation of free fatty acids along the reaction. The fatty soaps formed were in colloidal form partially soluble in the reaction products, and hence were required to be separated from the final product through several complicated filtration and separation processes. Furthermore, it was essential to maintain the anhydrous conditions in the system as the presence of alkaline catalyst can lead to irreversible hydrolysis of methyl ester to fatty acids. This has restricted the use of higher percentage of catalyst.

Heterogeneous calcium methoxide has offered slow reaction rate under the process developed by Gryglewicz *et al.* (2003) but it provided excellent results in some of the transesterification research works (Kouzo *et al.*, 2008; Martyanov and Sayari, 2008; Liu *et al.*, 2008, Masood *et al.*, 2012). The catalyst has the potential to achieve better TMPTE conversion with low soap formation. In addition, calcium methoxide showed less contribution to saponification in order to gain environmental feasibility and economic reliability. Performances of both heterogeneous calcium methoxide and homogeneous sodium methoxide in the synthesis of high oleic

TMPTE are shown in Table 6 (Chang *et al.*, 2012). The TMPTE yields and saponification after different time intervals were determined and compared. The results show 91.75% of Na⁺ was converted into soap at the end of reaction, while only 34.03% of Ca²⁺ got transformed into soap. This might be due to the homogeneous form of sodium methoxide with respect to reaction products but calcium methoxide remained solid throughout the reaction. For sodium methoxide, saponification reaction occurred spontaneously with ester and fatty acids as a competing reaction to the transesterification (Yunus *et al.*, 2003). However, transesterification and saponification had occurred on the surface of calcium methoxide resulting in a rather less conversion into soap. The amount of soap produced per gram of the reaction mixture after 10 hr. by calcium methoxide was 18 mg/g, which is much less than the amount of soap produced while employing sodium methoxide after 2 hr. under the same reaction conditions i.e. 46 mg/g (Figure 6).

Table 6 Contribution of Catalysts towards Saponification
(Chang *et al.*, 2012)

calcium methoxide			sodium methoxide		
time (hr.)	total soap (g)	catalyst conversion to soap	time (hr.)	total soap (g)	catalyst conversion to soap
1	0.54	10.56%	0.08	1.89	38.91%
2	0.86	17.01%	0.16	2.92	60.13%
3	1.11	21.77%	0.5	3.78	77.72%
4	1.15	22.69%	1	4.33	89.04%
6	1.39	27.25%	2	4.46	91.75%
8	1.64	32.18%			
10	1.73	34.03%			

Meanwhile, the yield of triester in case of calcium methoxide was 65.8% which is considerably less than 96.4% obtained by sodium methoxide. Sodium methoxide had reduced the mass transfer residence due to its homogeneous nature which led to good reaction efficiency but at the same time created more soap as compared to its heterogeneous counterpart. From these results, calcium methoxide has demonstrated an encouraging potential as the transesterification catalyst in the production of high oleic TMPTE, however, optimization is required to obtain reasonable reaction conditions.

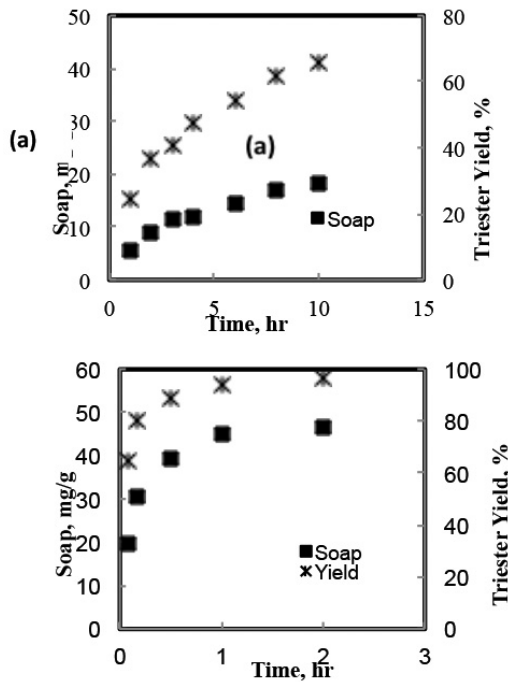


Figure 6 Amount of soap and yield of triester generated by: (a) calcium methoxide (b) sodium methoxide (Chang *et al*, 2012)

The results from the optimization study for the operating parameters using calcium methoxide catalyst is shown in Figure 7. The parameters are temperature, % catalyst, reactant molar ratio, and vacuum pressure. The samples were collected and analyzed to determine the composition of TMPTE by gas chromatography (Yunus *et al.*, 2002). It is evident that the yield of TMPTE was low at 140 °C and increased with temperature. Higher temperatures usually tend to reduce the reaction time for the transesterification reactions, but if the temperature is too high PME might evaporate resulting in the occurrence of a reverse reaction which eventually reduces the yield of TMPTE. Furthermore, higher temperature favors saponification to take place which lessens the activity of catalyst as well as the yield of TMPTE. The reaction was conducted for 8 hr.

In this study, on increasing the catalyst above 0.3% the yield of TMPTE remained more or less the same at around 97%. When homogeneous sodium methoxide was employed for transesterification of PME to TMPTE, 0.8% w/w catalyst was required to achieve 90% conversion to triester (Yunus *et al.*, 2003). However, in the current experimental conditions; the addition of 0.3% catalyst by weight of reaction mixture has resulted in an effective yield, and therefore can be regarded as an optimum value under these conditions. The effect of molar ratio of TMP: PME on the composition of TMPTE is also important. At the stoichiometric ratio of 1:3, a yield of 75% triester was obtained after 8 hr. reaction time. However, at TMP to PME ratio above 1:6, more than 98% yield of triester was achieved. Generally, a better product yield is obtained by keeping the molar ratio of reactants higher than the stoichiometric values since the reaction is driven more towards completion (Ramadhas *et al.*, 2005). However, the effect of excess reactant was hindered at molar ratios of 1:7.5 and 1:9. This probably

happens because the mass transfer has been constrained by the limited catalyst surface area for the reaction and therefore the yield is more or less the same as compared to 1:6. So, 1:6 can be considered as the optimum molar ratio.

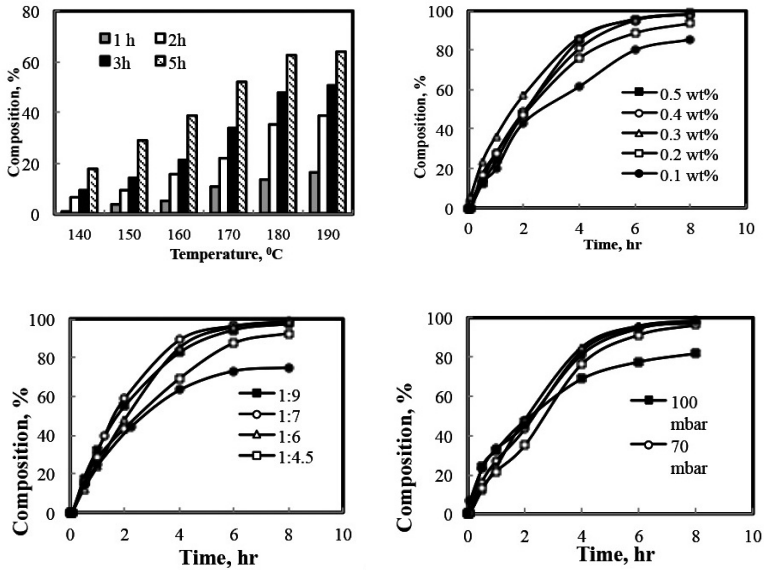


Figure 7 Effects of temperature, % catalyst, molar ratio and vacuum on TMPTE yield (Chang *et al.*, 2012)

The effect of vacuum on the rate of transesterification of TMP and PME was studied at 10 mbar, 20 mbar, 50 mbar, 70 mbar and 100 mbar, High vacuum facilitates the efficient removal of methanol from the system which in turn favors the forward reaction. However, high vacuum requires high energy and high equipment cost for industrial scale processing plant, especially when vacuum level has to go below 20 mbar. At vacuum level below 20 mbar, vacuum booster (special high energy consumption equipment) is normally required. Secondly, higher vacuum level reduces the boiling point

of the PME. At 4.9 mbar, the boiling point of methyl oleate (C18:1) is approximately 175 °C as predicted using Antoine equation. From 50 mbar to 10 mbar, only small change in product yield was observed due to the limitation of process and phase equilibrium between methanol and ester. Therefore, 50 mbar is regarded as the optimum vacuum for the system which produces reasonable yield of TMPTE and ensures the feasibility for industrial practice.

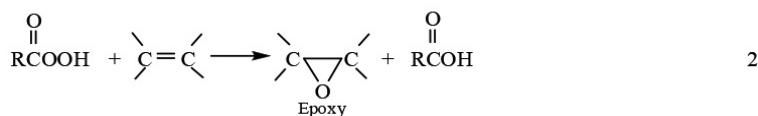
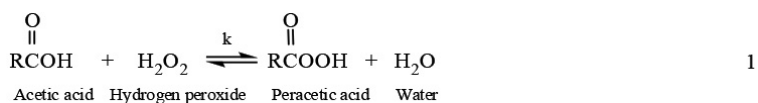
The quantity of saponification generated by the heterogeneous calcium methoxide was determined by utilizing the optimum experimental conditions investigated in the previous section, for the transesterification between TMP and high oleic PME. Almost 52% of calcium methoxide got converted into soap at the end of 8 hr. reaction time, and at the same point the yield of TMPTE was more than 98%. In contrast to sodium methoxide under its respective optimum conditions for this transesterification reaction, calcium methoxide showed markedly lower tendency to transform into soap. Judging by the amount of catalyst used at the start of reaction, 0.3% w/w calcium methoxide producing 9.2 mg soap/g of product at the end of reaction seems to be a more appropriate choice for transesterification as compared to 0.9% w/w sodium methoxide producing 46 mg/g soap. Finally, 0.3 w/w% calcium methoxide generated almost the same yield of TMPTE at the end of the reaction as obtained by higher amount of sodium methoxide under optimum conditions (Chang *et al.*, 2012).

Epoxidation of TMP Ester

Improving the oxidative stability properties of bio-based lubricants (biolubricant) is important in maintaining the sustainability and performance of the lubricants. Oxidative stability of a lubricant is very much related to the level of unsaturation in the oil as the the double bond provides a vulnerable site for the oxidation reaction.

One of the ways to eliminate the double bonds is by epoxidation reaction with oxidizing agent in which the double bond is converted into an oxirane ring (Naidir *et al.*, 2012). In this study, the palm oil-based synthetic lubricant, chemically known as trimethylolpropane (TMP) ester was epoxidized using an *in-situ* peracid process. An *in-situ* peracid acid process was chosen mainly due to safety reasons (Goud *et al.*, 2007). The concentrated peracid is unstable and explosive if it were to be generated externally.

Epoxidation reaction is a reversible reaction during which peracetic acid is formed *in-situ* from hydrogen peroxide and acetic acid catalyzed with a suitable catalyst. The reaction then proceeds concurrently with the epoxidation of the ethylenic unsaturation (double bond) of the TMP ester. Consequently, the peracetic acid is converted back to acetic acid for further reaction with the hydrogen peroxide to form more peracetic acid for subsequent epoxidation process. This process continues until the hydrogen peroxide is completely consumed or until the ester is completely epoxidized (Niederhauser and Koroly, 1949). Finally, the ethylenic unsaturation in TMP ester will all be converted directly to the oxirane ring. The formation of peracetic acid from the reaction between acetic acid and hydrogen peroxide is relatively slow so a strong acid catalyst is needed to produce the high yields of oxirane ring as a final product. The type of catalyst can be homogeneous or heterogeneous. However, in this kinetics study, homogeneous catalyst was applied. The *in-situ* epoxidation process was chosen and the mechanism of an *in-situ* epoxidation in the presence of a homogeneous catalyst is generally represented in the Scheme 2.



Scheme 2 *In-Situ* Peracetic Acid Process in Epoxidation Reaction

The effects of reaction time at various temperatures are shown in Figure 8 (Naidir *et al.*, 2012). At higher temperatures, the rate of reaction is very fast as evidenced from the slope of the curves thus require shorter time to achieve a complete reaction. The epoxidation reaction at lower temperatures reached the maximum conversion of oxirane oxygen in more than 4 hours, while at higher temperatures it was achieved in less than 1 hour. Since the rate of reaction for the low temperature region is very much slower compared to high temperature region, the reaction kinetics was divided into two temperature regions, namely low temperature (30, 50, and 60°C) and high temperature (70, 80, and 90°C).

The epoxidized TMP ester showed marked improvement in lubricating characteristics compared to TMP ester. The oxidative and thermal stability was determined using turbine oil oxidation stability test (TOST) equipment following the ASTM D943 standard test method. Lubricating oil will oxidize when the oil is exposed to air, particularly at high temperatures. This has a very strong affect on the life of the oil. In TOST, the life time is determined from the acid number of samples test. The results of oxidation life time of TMP esters and epoxidized TMP esters were obtained at 6.4 and 2.9 of acid number respectively which is the values reached

after 500 h operation (Naidir *et al.*, 2012). This indicates that the epoxidized TMP ester has shown considerable improvement in oxidative stability over TMP esters. Although the value of pour point is marginally higher but other lubrication properties such as kinematic viscosity, VI, wear and friction properties are better than the properties of most vegetable oil-based commercial base oils.

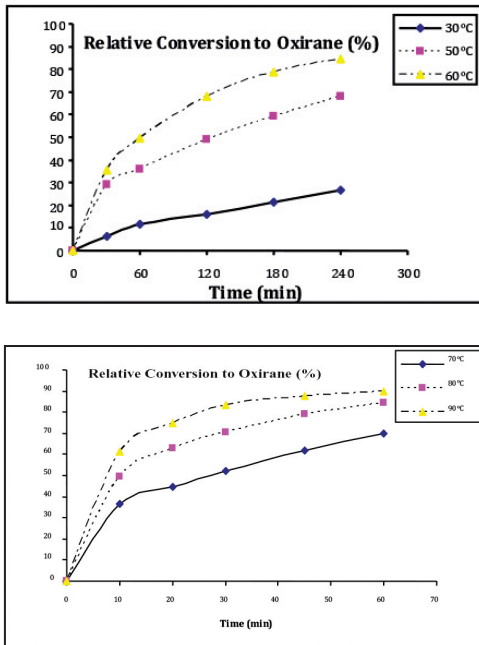


Figure 8 Effects of Temperature and Time on Relative Conversion to Oxirane at (a) Low Temperature Region and (b) High Temperature Region (Naidir, *et al.*, 2012)

APPLICATIONS OF PALM OIL-BASED TMP ESTERS

Palm Oil-based TMP as Industrial Metalworking Fluid

The ester content, characteristics and physical properties of the HO-TMPTE used as the base oil in the formulation of metalworking fluid are summarized in Table 7 (Chang *et al.*, 2012). The properties are compared to the commercial TMPTO and Radialube 7561. TMPTO is usually synthesized via chemical esterification reaction using TMP and oleic acid.

Tapping oil or metalworking fluid formulated using the high oleic trimethylolpropane ester (HO-TMPTE) were studied in term of physical properties, stability and performances in thread tapping application (Chang *et al.*, 2012). The results obtained from this study are summarized in Table 8. In this work, three tapping oil formulations were prepared and then compared against the pure HO-TMPTE (without any additives, TO-A) and the commercial petroleum-based tapping oil, namely New Rapid Tap (TO-E). Tapping process for internal thread in the metalworking industries is one of the most challenging operations usually due to breakage of the costly taps as well as the wasted metal work piece. Ideally, all tapping oil formulations should have a clear and homogeneous mix showing good compatibility between all additives. In some cases, solid phase additives are added as the AW and EP additive. However, it must maintain a stable suspension over certain years of storage. Among the prepared formulations, TO-D and TO-E were prepared using liquid phase EP, AW and lubricity additives. Oil mix compatibility test showed that these two formulations remained clear and stable under different storage temperatures, thus the additives were considered compatible with HO-TMPTE in the tapping oil formulations.

Table 7 Characteristics and physical properties of the HO-TMPTE and the commercial TMP trioleate (Chang *et al.*, 2012)

Properties	HO-TMPTE	Radialube 7561	TMPTO-A
Esters composition (% w/w)			
Methyl esters*/fatty acids**	5.1*	0.4**	2.3**
TMP monoesters	0.2	0.7	-
TMP diesters	10.2	3.8	6.1
TMP triesters	84.5	95.1	91.6
Soap Content (mg/g) ^a	2.49	0.02	0.02
Fatty acid compositions (% w/w)			
C16	1.8	6.4	4.9
C18	1.8	0.9	0.9
C18:1	86.8	78.3	81.8
C18:2	8.7	5.9	1.5
C18:3	0.3	6.1	9.4
Others ^c	0.6	2.4	1.5
Characteristics and Physical Properties			
Pour Point (°C)	-30	-36	-39
Flash Point (°C)	270	306	260
Cloud Point (°C)	0	-3	-6
Density at 20°C (g/cm ³)	0.914	0.928	0.917
Viscosity at 40°C (mm ² /s)	44.3	46.3	47.9
Viscosity at 100°C (mm ² /s)	9.9	9.3	9.8
Viscosity Index	219	189	196
Acid Value (mgKOH/g)	0.28	0.46	2.97
Demulsibility ^b	60 min 5/38/37	< 30 min	< 30 min

^a Measured in mg of soap in oleate per gram of sample

^b Demulsibility time limit at emulsion reduction to 3 ml was set at 30 min. Reported as < 30 min if the time limit was fulfilled otherwise the volume of oil/water/emulsion remaining at the reported time in ml

TO-C was prepared with microcrystalline boron nanoparticles, namely BD-0908 and it functioned as EP as well as AW additive in the formulation. Due to the presence of the solid nanoparticles phase, the oil preparation appeared to be hazy at room temperature. Further testing on the storage stability of TO-C at 5°C for 24h resulted in slight fallout of the nanoparticles at the bottom. Commercial tapping oil, New Rapid Tap (TO-A) examined in this work is a mineral-vegetable oil mixed oil with a viscosity of 30.1 mm²/s at 40°C. The viscosities of other tapping oils formulated with HO-TMPTE were higher than the commercial one because the base oil itself was ISO46 grade base oil. Densities of the oils were also measured as indicative parameters. TO-A has a density of >1.0 g/cm³ at 20°C indicated that the oil was blended with high percentage of high molecular weight, polymerized oils as well as mineral based EP and AW additives, however the details of the additives involved were not known.

Table 8 Properties of the formulated high oleic palm based TMP triesters tapping oils (Chang *et al.*, 2012)

Properties	Tapping Oil ^a				
	TO-A	TO-B	TO-C	TO-D	TO-E
Appearance	Amber, Clear	Yellow, Clear	Brown, slight cloudy	Amber, Clear	Amber, Clear
Viscosity at 40°C (mm ² /s)	30.1	44.3	49.6	58.7	52.4
Density at 20°C (g/cm ³)	1.004	0.914	0.918	0.922	0.941
Temperature stability					
At 5°C	No separation	No separation	Partial separation	No separation	No separation

At room temperature	No separation	No separation	No separation	No separation	No separation
At 50°C	No separation	No Separation	No separation	No separation	No separation
Field tapping test performance on SS304 plate ^b					
1/4" BSP Tap	Passed	Passed	Passed	Passed	Passed
3/8" BSP Tap	Passed	Failed	Passed	Passed	Passed
1/2" BSP Tap	Passed	Failed	Passed	Passed	Failed*
Field tapping test performance on mild steel plate ^b					
1/4" BSP Tap	Passed	Passed	Passed	Passed	Passed
3/8" BSP Tap	Passed	Failed	Passed	Passed	Passed
1/2" BSP Tap	Passed	Failed	Passed	Passed	Passed

^a TO-A, New Rapid Tap, commercial tapping oil; TO-B, HO-TMPTE only as control; TO-C, TO-D and TO-E, formulated tapping oil with HO-TMPTE as in Section 2.3.

^b 'Passed' indicates successful tapping through all 5/5 of holes on the plate, "Failed*" indicates unsmooth tapping with successful tapping only through 4/5 of holes on the plate and 'Failed' indicates jammed tapping for > 1 hole on the plate.

As far as the field thread tapping test was concerned, TO-A, TO-C and TO-D formulations are able to meet the testing conditions as set. TO-B which was applied directly without adding any additives passed the 1/4" BSP thread on the 12.7 mm SS304 plate, however it failed for 3/8" and 1/2" thread on both SS304 and mild steel plates. TO-C showed good performance for all tapping tests indicated that BD-0908 was an effective EP/AW additive when blended together with HO-TMPTE. TO-D and TO-E were formulated with different degrees of AW and EP treatments. TO-D was formulated as a heavy duty formulation suitable for applications in hard metals like stainless steel, duplex stainless steel, hastelloy[®] etc. Conversely, TO-E was prepared as a light duty formulation. It did not work perfectly on the SS304 even though GY-115 contains sulfur compound as the sulfur present was in passive form

(sulfurized-vegetable oil), thus the EP/AW effects was relatively lower. This formulation was suitable for light duty applications like thread tapping on carbon steel, mild steel, aluminum, brass etc. Sulfur additive on the other hand is known to create staining effect on the yellow metals (copper containing metals and alloys). Hence, KSP-93 metal deactivator was added as detergent to prevent the potential staining. In this work, 360-P was added into TO-D and TO-E as EP/AW supplement to the sulfur-base additives (Chang *et al.*, 2012).

Palm Oil-based TMP as Hydraulic Fluid

Hydraulic fluids represent one of the most important groups of industrial lubricants. The consumptions of hydraulic fluids in the US are at approximately 5 million metric tons per year [Lawate, 2002], and have the highest need for biodegradable lubricants. Although vegetable oil-based hydraulic fluids are gaining popularity, the lubricating properties of vegetable oil, such as poor oxidative stability and high pour point, have hindered their use. This unsatisfactory performance curbs their more widespread utilization as lubricants. Malaysia as the world largest exporter and producer of palm oil, have abundant raw material supply of palm oil.

We investigated the potential of using palm oil-based trimethylolpropane ester (TMPTE) as the base oil for hydraulic fluid application (Alias *et al.*, 2009). It is suspected that the oxidative stability of unadditived base oil will be deteriorating after prolong exposure to heat and shear. Viscosity is one of the most important properties for characterization of lubricants and their transport properties and it is a measure of internal friction in a fluid. On the other hand, the acidity of used oils is of interest to measure the degree of oxidation of the fluid (Eisentraeger *et al.*, 2002). Thus, both viscosity and TAN have been chosen to describe the degree of aging of the hydraulic fluids. Hence, the effects of additives A and B on oxidative stability of additived oil were examined at various

operating temperatures. The analysis of oxidative stability of the oil via total acid value determination is critical to assess the suitability of TMPTE base oil as the base fluid. Finally, the properties of formulated lubricant are compared with the properties of hydraulic fluids formulated using Refined Bleached and Deodorized Palm Oil (RBDPO) base oil. The results from this investigation are shown in Figure 9 (Alias *et al.*, 2009).

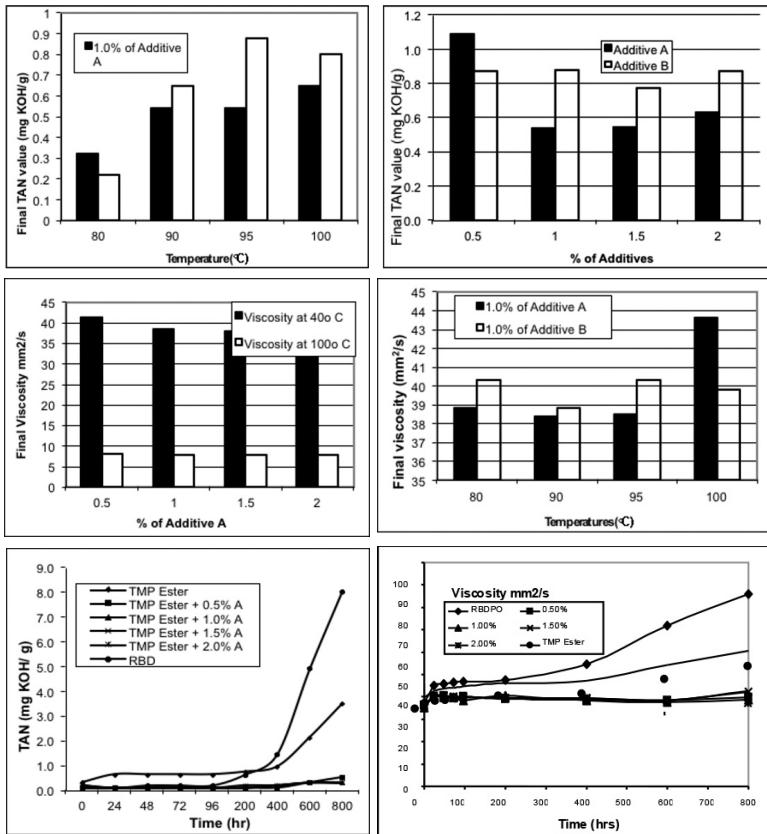


Figure 9 Effects of additives on hydraulic performances (Alias *et al.*, 2009)

The oxidative stability of the oil was evaluated by total acid number (TAN) and viscosity tests. In general, base oil without additive began to degrade after 200 h. The formulated oil, on the other hand, was quite stable even after 800 h of operation. The best formulation was obtained using 1.0% of either additive A or additive B. Both TAN and viscosity values were found to increase with increasing heating temperature. Meanwhile, the results have also shown that additive A performs better than additive B. After 800 h of exposure, the final TAN value for the formulated oil was only at 0.32 as compared to 4.88 mg KOH/g for the oil without additive. However, the kinematic viscosity of the oil at 40 and 100 °C was almost unchanged as compared to the oil without additive. From the results, it can be concluded that the best formulation of the hydraulic fluid was achieved by adding 1.0 % of additive A into the TMPE base oil. The maximum working temperature was at 95°C. With this formulation, the changes in TAN was only marginal, viscosities at 40°C and 100°C were almost unchanged, while VI value remained at 187. However, additive B was found to be more suitable at higher operating temperatures (Alias et al., 2009).

Palm Oil-based TMP Ester in Engine Oil

Palm oil-based TMP ester has also being tested in engine oil. The wear performance of engine oil prepared by adding certain percentages of palm oil-based TMP esters to the commercial lubricant are investigated (Zulikfli *et al.*, 2014a,b). The major function of engine oil is to decrease the frictional force, by forming a thin film between the moving parts in the engine such as piston and cylinder. Consequently, wear of the moving parts is reduced and diminished the power loss. Besides, engine oil is also used to

cool the engine by carrying away the heat, inhibits corrosion, cleans and improves sealing.

One of the most important properties of engine oil is viscosity, which should be high enough to maintain the lubricating film thickness, and low enough to make sure the oil can flow through all the engine parts. Only the development of low coefficient of friction lubricant and surface development is the solution to reduce this energy consumption. Hence, in order to have a better understanding of reduction of frictional forces through the tribological study, a new type of lubricant substitute TMP is introduced. The effects of TMP ester on different lubrication regime using four-ball machine and HFRR (high frequency reciprocating machine) wear tests have been investigated. The results from this study on the tribological properties under boundary and hydrodynamic lubrication for the blends of palm-oil based TMP esters and ordinary lubricants are shown in Figure 10 (Zulikfli *et al.*, 2014a,b).

The experimental results show that palm oil-based TMP ester based lubricant improves the wear preventive lubrication properties in terms of CoF and WSD. The TMP 3 (3%TMP, 97% commercial lubricant) shows the lowest WSD and CoF with compared to others lubricants analyzed in this study. In addition, under extreme pressure condition maximum load bearing capacity of 220kg, TMP 3 blend retains its quality without breakdown. Under the fluid film lubrication using reciprocating test TMP 7 shows the best lubricity property with the lowest friction torque. Nonetheless, in order to utilize palm oil-based TMP ester as engine oil, many other properties including oxidative, thermal and hydrolytic stabilities need to be examined. Palm oil-based TMP ester is environmentally desired to mineral oil-based lubricants, research to investigate the properties of palm oil-based TMP ester to make it technologically competitive as automobile lubricant, and should be encouraged.

Biobased Lubricants: Harnessing the Richness of Agriculture Resources

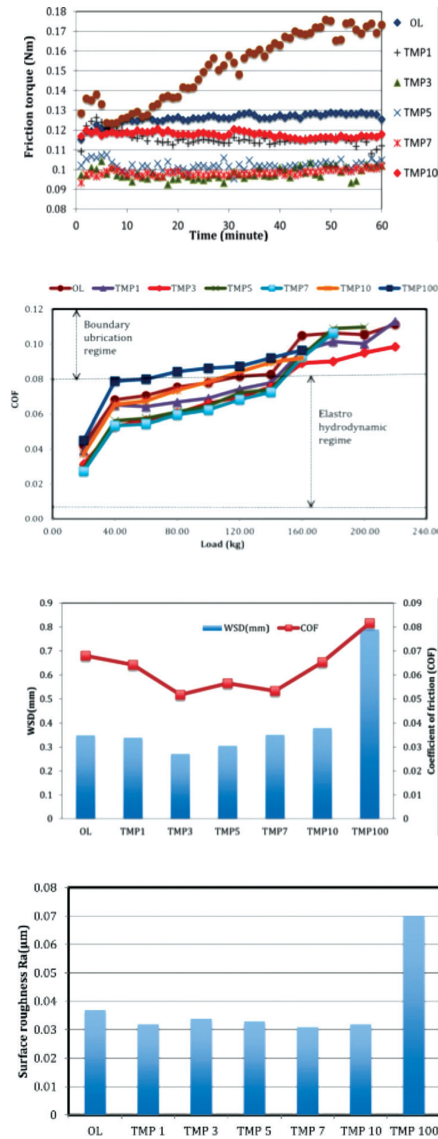


Figure 10 Wear prevention characteristics of a palm oil-based TMP ester as an engine lubricant (Zulikfi *et al*, 2014a/b).

BIOLUBRICANT FROM PENTAERYTHRITOL ESTER

Introduction

Food grade lubricants are mostly produced from refined naphthenic mineral oil or white oil, which are not promisingly safe-based oils. Mineral oil-based lubricants are harmful to human beings and the environment, and also there is another issue of its poor biodegradability and toxicity which has led to health problems on a long term basis (Willing, 2001; Oluyor and Ori-jesu, 2009). In response to the regulation of the National Sanitation Foundation (NSF), only H1, H2, and H3 types of food grade lubricant-based oil are allowed to be used in the food processing industry. H1 are food grade lubricants applied in the food processing environment where there are possibilities for the lubricant coming into contact with food. Food grade lubricants from the H2 group are used at areas of no food contact possibility, such as on equipment and machine parts. H3 food grade lubricants that are used to prevent rust on equipment like hooks and trolleys are from edible oil.

Neopentyl polyol ester proved to be better than the other ester with its excellent thermal and oxidative stability, enhanced lubricity, viscosity, viscosity index and better biodegradability (Eychenne *et al.*, 1998; Chang *et al.*, 2012). Pentaerythritol is a polyol with four –OH group, thus the tetraester of pentaerythritol is envisaged to have the properties suitable for food grade lubricant. However, there is little information reported on the potential of aliphatic pentaerythritol ester as a lubricant. The knowledge of the pentaerythritol molecular structure and its viscosity-temperature properties have not been studied in detail. In this research work, the polyol of pentaerythritol was modified to the palm oil chemical structure without the hydroxyl pentaerythritol group. The

transesterification reaction parameters were optimized and various interaction parameters were also investigated by using response surface methodology (RSM). Moreover, some characterization of tetraester was also performed.

Further study was made through formulating the base oil which was by adding anti wear and corrosion inhibitor additives. These additives such as Irgalube 349 and Irgalube TPPT (antiwear), Irgamet 39 and Sarkosyl O (corrosion inhibitor) were approved by Food and Drug Administration (FDA) and United State Department of Agriculture (USDA). The formulated base oils undergone various properties testing, such as kinematic viscosity, viscosity index, pour point, copper strip corrosion and four-ball test. The result is then compared with commercial lubricant (CL) available in the market.

Synthesis of Palm Oil-Based Pentaerythritol Ester

The synthesis of palm oil-based pentaerythritol was carried out using the low-pressure method (Aziz *et al.*, 2014). The alkaline catalyst was preferred as it accelerated the reaction faster and it is non-toxic compared to some other acid catalysts (Yunus *et al.*, 2003a). Application of sodium methoxide also requires intensive care, such as the reaction should be maintained under an anhydrous condition. The reaction scheme showing the reaction between palm methyl ester and pentaerythritol is shown in Figure 11.

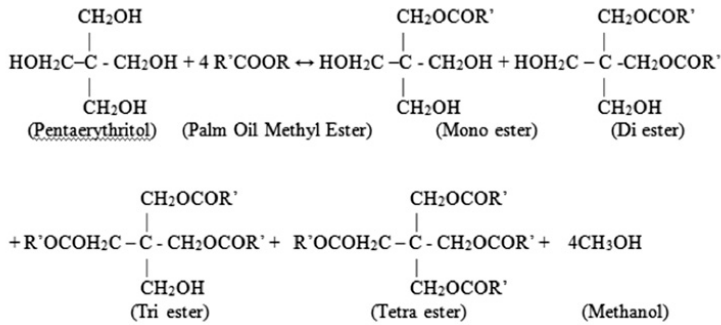


Figure 11 Transesterification reaction of PEE

An experimental design for the experiment with five levels and four factors (temperature, amount of catalyst, palm oil methyl ester-to-pentaerythritol molar ratio, and reaction duration) was selected. The response surface methodology (RSM) suggested that the optimized conditions for the high yield composition of pentaerythritol ester were the reaction temperature of 158 °C, amount of catalyst of 1.2 wt.%, molar ratio of 4.5:1 and reaction time of 60 min. The predictor estimated that the highest pentaerythritol ester yield that could be achieved with these conditions was 40.1%. After a triple run of experiments, it was found that the actual yield of pentaerythritol tetra ester or pentaerythritol ester (PEE) obtained at the optimum variable condition suggested was 37.6% with a tolerance of 6% representing the repeatability of the process optimization condition.

Figure 12a shows a plot of the process variables that give the most significant impact to the fitted model which was the interaction between the catalyst and molar ratio. It could be seen that increasing the catalyst concentration and molar ratio significantly increased the PEE composition. The increment of temperature and catalyst

raises the pentaerythritol ester (PEE) composition as shown in Figure 12b. The amount of catalyst gave a positive increment of the PEE composition. Nevertheless, at a high temperature, there was an increment of the PEE composition which resulted from the methanol produced from the reaction.

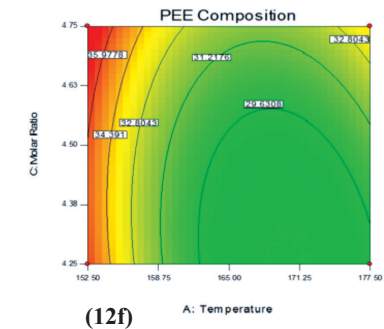
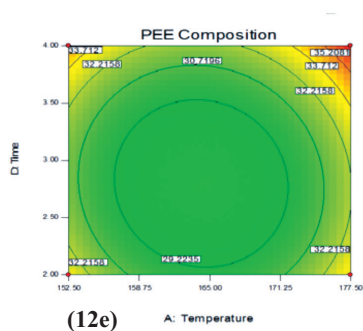
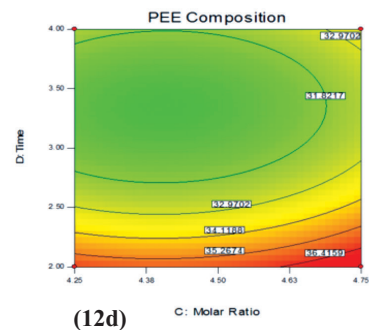
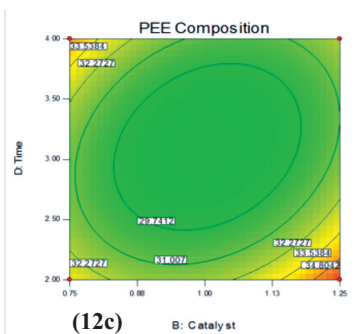
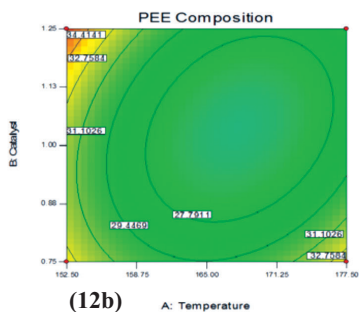
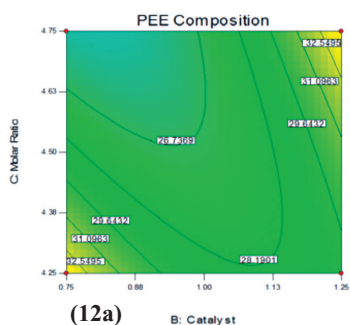


Figure 12c depicts the interaction between the catalyst and the reaction time, and the PEE composition decreased along the increment of time due to some product being reversed. A large amount of catalyst could promote the production of fatty acid. If water or moisture in the oil content reacted with methyl ester, fatty acid was formed and led to fatty soap development in the presence of a metal catalyst (Yunus *et al.*, 2003a). Due to this reason, it affected the production of PEE. The effect of molar ratio with time, temperature with time, and temperature with molar ratio as shown in Figure 12d, 12e, and 12f had a moderate impact contributing to the fitted model.

Figure 13 shows the GC analysis for the PEE ester and commercial sample from China (Watercare Chemicals (Suqian) Co. Ltd.),

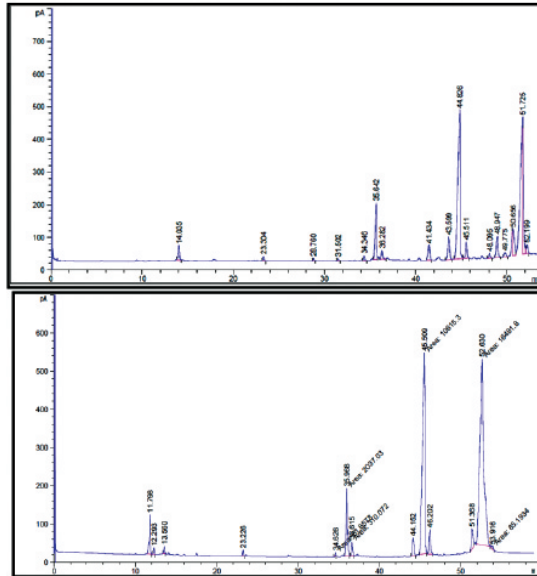


Figure 13 Gas chromatography analysis of synthesized PEE and commercial PEE (Aziz *et al.*, 2014)

Table 9 depicts the properties of the PEE produced that surpassed the temperature resistance of the commercial pentaerythritol tetraoleate (PETO) and trimethylolpropane ester (TMPTE) properties (Yunus *et al.*, 2005). The kinematic viscosity of PEE is relatively higher than TMPTE and more suitable for an oven chain application.

Table 9 Comparison of base oil properties (Aziz *et al.*, 2014)

Properties	Standard	PEE ^a	PETO ^b	TMPTE ^c
Kinematic Viscosity @ 40°C (cSt)	ASTM D445	68.4	65.9	49.7
Kinematic Viscosity @ 100°C (cSt)	ASTM D445	12.7	11.9	9.8
Cloud Point (°C)	ASTM D2500	9	-11	Not stated
Pour Point (°C)	ASTM D97	<-20	<-35	-1
Flash Point (°C)	ASTM D93	302	246	Not stated

^aPEE, pentaerythritol ester, ^bPETO, commercial pentaerythritol tetra oleate, ^cTMPTE, trimethylolpropane ester from Yunus *et.al.* (2005) data.

Palm Oil-based Pentaerythritol Ester as Food Grade Oven Chain Lubricant

Pentaerythritol ester that was used as base oil has the following properties; viscosity, 72.78 cSt at 40°C and 13.08 cSt at 100°C, composition of 42.75 % of tetraester, 41.27 % of triester, 12.12 % of diester, 0.51 % of monoester followed by 3.35 % of palm oil methyl ester. Additives were added at different composition and combination to enhance the wear and corrosion resistance properties of synthesized base oil. (Table 10).

Table 10 Oven Chain Formulation (*Aziz et al.*, 2014)

Item	AWCI 1	AWCI 2	AOAWCI	AOAWCI 2
PE	99.6	99.45	99.1	98.95
Irganox L57	0	0	0.5	0.5
Irgalube 349	0.15	0.15	0.15	0.15
Irgalube TPPT	0.15	0.15	0.15	0.15
Irgamet 39	0.1	0	0.1	0
Sarkosyl O	0	0.25	0	0.25
Total	100	100	100	100

Iodine value was an indication of unsaturated component in the lubricant. High value of iodine value denoted high unsaturated component in the substance. Commercial lubricant from Klüberfood NH1 CH-2 Plus (CL) had the lowest iodine value, which indicates that the lubricant is more saturated compared to the formulated lubricant. From the results, both AWCI and AWCI 2 had high iodine value which were 90.07 and 91.96 respectively, however, after addition of antioxidant, the value decreased to 85.21 and 78.47 respectively (Table 11). It could be conclude that antioxidant used (Irganox L 57) structure contain less double bond that reduce the iodine value when mixed to the base oil.

Table 11 Properties of Food Grade Lubricant (Aziz *et al.*, 2014)

Formulation	Base oil	AWCI 1	AWCI 2	AOAWCI 1	AOAWCI 2	CL
Iodine Value (IV)	80.67	90.07	91.96	85.21	78.47	5.18
Total Acid No. (TAN) mg KOH/g	0.2	0.41	0.41	0.61	0.41	0.61
Kinematic Viscosity @ 40 °C, cSt	72.78	75.37	76.08	73.48	74.15	75
Kinematic Viscosity @ 100 °C, cSt	13.08	13.16	13.2	12.94	13.09	11
Viscosity Index (VI), cSt	148	143	142	143	143	126
Pour Point, °C	-21	-19	-19	-19	-19	-18
Cloud Point, °C	8	6	6	6	6	-1
NOACK Volatility (%)	1.7	2.2	1.4	2	1.4	2

The total acid number of the base oil was the lowest at 0.2 compared to other lubricant (Table 11). Commercial lubricant and formulation AOAWCI 1 total acid number were 0.61. As expected, commercial lubricant gave highest pour point which was -18°C with agreement of its lowest iodine value. Base oil gave lowest pour point, -21°C while others were -19°C . Cloud point of commercial lubricant was the lowest -1°C leaving others behind. From the kinematic viscosity only two formulations surpass commercial lubricant viscosity (75 cSt) were AWCI 1 and AWCI 2 with 75.35 and 76.08 cSt at 40°C . AWCI 2 and AOAWCI 2 showed smallest percentage of NOACK volatility, 1.4 % compared to other lubricants. The formulated lubricants were found to be improved in term of coefficient of friction (Table 12). Lower coefficient of friction resulted to lower WSD. From copper strip corrosion test, the best formulation AWCI showed pass result using copper plate which undergone slight tarnish (1a) (Figure 14). Whereas other formulated lubricants including commercial lubricant depicted that the copper plate tarnish from moderate to dark. From these results, it could be concluded that AWCI 1 is the best formulation which is comparable to commercial lubricant in term of corrosive resistance, coefficient of friction, viscosity and pour point.

Table 12 Wear performance of lubricants (Aziz *et al.*, 2014)

Lubricant	A	AWCI 1	AWCI 2	AOAWCI 1	AOAWCI 2	CL
Coefficient of Friction	0.085	0.091	0.082	0.092	0.103	0.101
Wear Scar Diam. (mm)	0.5	0.3044	0.3136	0.3178	0.3380	0.2813

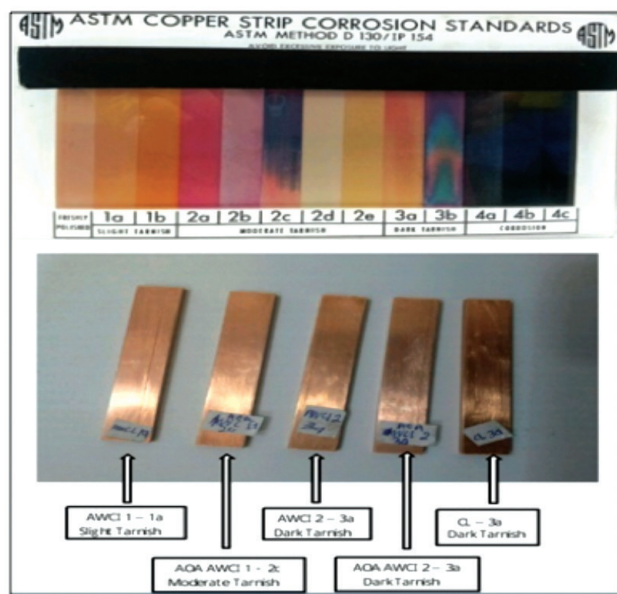


Figure 14 Copper Corrosion Test Result (Aziz *et al.*, 2014)

DRILLING FLUID FROM 2-ETHYLHEXYL ESTER

Introduction

Drilling fluid is defined as a blend of chemical and natural compounds pumped and flowed through drill pipe after passing through bit nozzles, finally carrying rock cuttings from subterranean well hole to the surface through the annular space between the drill pipe and the hole wall as shown in Figure 15 (Nasiri *et al.*, 2009). Generally, the composition of drilling fluid consists of a base fluid as the continuous phase and various kinds of additives. The kinds and amounts of these additives as well as the conditions of wells determine the formulation for drilling fluid of which enables the fluid to carry rock cuttings from beneath well to the surface, to cool and lubricate the bit, to control the stability of bore, to clean the

wellbore and form a thin, low permeability filter cake that prevents fluids (oil, gas and water) from penetrate through permeable rocks (Outline, 2011). The correct choice of drilling mud compositions affects both the rheological behavior and the success of drilling. Basically, drilling fluid could be differentiated by the Oil Based Mud (OBM), Water Based Mud (WBM), Synthetic Based Mud (SBM), Invert Emulsion Mud (IEM), air, foam fluids, etc (Shah *et al.*, 2010). WBM and OBM are the main types of drilling fluids.

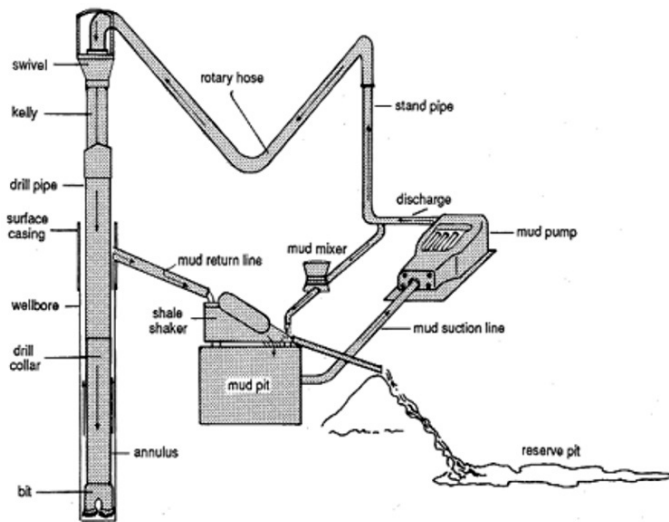


Figure 15 Drilling operation system and circulation of drilling fluid (Nasiri *et al.*, 2009)

Since 1990, the oil and gas industry has been using synthetic-based fluids (SBF) for the difficult drilling wells with reduced environmental impact (Caenn and Chillingar, 1996; Kamis *et al.*, 2000). SBF provides the drilling performance characteristics similar to traditional fluids made from diesel and mineral oil but safer to workers. The use of vegetable oil-based ester as a base

fluid in synthetic drilling fluid (SBF) has become a trend in drilling operations due to its environmental advantages. Ester-based oil is a nontoxic substitute for diesel in drilling oil or gas wells. Ester-based oils with different viscosities were synthesized using various types of vegetable oil-based methyl esters. This is vital as the requirement for the drilling fluid base oil is that the oil must have a viscosity below 5 mm²/sec. In our work we synthesized two types of esters, namely C12 ME ($\mu = 2.3$ mm²/sec) and 2-EH C12 ester ($\mu = 5$ mm²/sec) as base oils.

Synthesis of 2-Ethylhexyl Ester

In this reaction, vegetable oil-based methyl ester (ME) reacts with 2-ethylhexanol to produce the desired ester (Abdul Habib *et al.*, 2014). This transesterification reaction is a single step reaction because only one of the active sites is involved for the hydroxyl molecule to react with carboxyl group. Experiments were conducted to determine the optimum conditions of the transesterification reaction of methyl ester, ME and 2-ethylhexanol, EH. The reaction was carried out according to the procedures described by Yunus *et al.*, (2003). The sodium methoxide was held constant at 2% w/w, molar ratio of ME to EH at 1:2, and pressure at 1.5 mbar during the reaction. The results showed in Figure 16 clearly indicates that the reactions were very fast and almost completed after 7 minutes of reaction. These results also show that the temperature has marginal effect on reaction conversion within the selected temperature range. At these temperatures, almost 85% conversion was achieved during the first minute of reaction and after 7 minutes the reaction had already reached the completion.

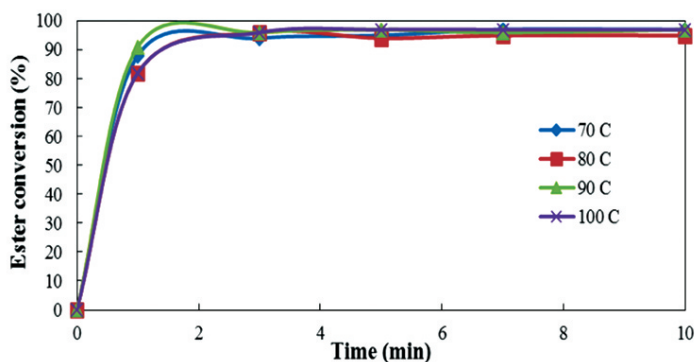


Figure 16 2-Ethylhexyl ester conversion vs time of the reaction (Abdul Habib *et al.*, 2014)

Ester-Based Drilling Fluid

The performance of the new base oils in drilling fluid formulation was assessed based on its rheological properties, electrical stability and filterability. Table 13, 6.1, 6.2 and 6.3 show the formulations used in this study, the mud density was 12 Ib/gal (1.44 g/cm³), oil to water ratio at 85/15 using two base oils, C12 ME and 2-EH C12 esters. Table 14 contains the formulations which were designed to compare the performance of C12 ME base oil (commercial oil) and the synthetic base oil of 2-EH C12 ester. To improve the loss of filtration after hot rolling at 250°F (121°C) for 16 hours, fluid loss agent, primary emulsifier, lime and the viscosifier were added to samples 2 and 3 as shown in Figure 17. Samples 3 and 5 showed acceptable rheology and filtrability for 6 rpm, 3 rpm (7-12 Low shear rate), Pv, Yp and loss of filtration. Additive type 2 was used to formulate and stabilize the samples (6-15) at 350°F after hot rolling at 300°F (149°C) as in Table 14. Figure 18 demonstrates the difference of fluid loss for C12 ME base oil and 2-EH C12 ester base oil. In spite of the unique rheology of samples 7, 8 and 10;

the amount of filtrate was high. This may be due to the hydrolysis of fatty acid ester to its components (fatty acid plus alcohol) under high temperature and the presence of lime that may activate the emulsifier system.

Figure 18 highlights the stability of 2-EH C12 ester and its satisfactory rheological properties compared to C12 ME after hot rolling at 300°F (149°C). Data for muds samples (11-15) of 2-EH C12 ester base oil have been prepared with an increase in secondary emulsifier type 1 (6 to 8g) in order to ensure all water droplets are coated with oil to reduce surface tension between water and oil. The samples also used advanced additives of viscosifier (1, 1.25, and 2 g) and fluid loss agent type 2 (12, 15 g). Consequently, sample 15 was very stable before and after hot rolling with just 2 ml of filtration and 1.5 mm of mud cake thickness. Figure 19 depicts the comparison between 2-EH C12 ester muds (samples 13 &15) and Nasiri *et al.*, 2009 (samples 26 &27), which indicates that Pv of 2-EH C12 ester is comparable to Nasiri at 300°F(149°C). For Yp, 2-EH C12 ester is better than Nasiri; thus, 2-EH C12 ester can carry the cuttings better. The filtrate amount of 2-EH C12 ester was less than Nasiri's formulation even though the base oil used by Nasiri was blended with LAO (linear alpha olefin) to reduce its kinematic viscosity.

For 350°F (177°C) aging temperature, 2-EH C12 ester was formulated with ultra-advance (type 3) additives (viscosifier and fluid loss agents) that are stable up to 450°F (232°C). Sample 16 used emulsifier system type 2 and sample 17 was mixed with fluid loss agent type 2 to improve the rheology. However, the rheology of sample 17 was still poor; it failed to suspend and carry the weighting agent particles as shown in its gel strength @10 sec and @10 min and in 6 and 3 rpm. Figure 20 shows the

comparison between Nasiri *et al.*, 2009 samples (34 and 35) and 2-EH C12 ester samples (17 and 18) at 350°F(177°C). The HTPH filtration test was done at 350°F (177°C) and 500 Psi of pressure. For temperatures above 400°F (204°C), the tests were done at hot rolling temperatures. Samples (20-23) in Table 16 were aged at 412°F (212°C), formulation number 21 is same as 20 whereas 2-EH C12 ester @ 412°F (212°C) hydrolyses under excessive of calcium hydroxide (Lime=5 g). Muds of (21, 22 and 23) were prepared with 2 g of lime, (1 and 1.5g) of viscosifier and (5 and 6g) of fluid loss agents. Rheological characteristics of 2-EH C12 ester based muds were assessed for the adequate formulation data under hot rolling temperatures (250, 300, 350 and 412F) (121, 149, `177, and 212°C) as shown in Figure 21. It is clear that the rheology was improved when hot rolling temperature was increased for two reasons, firstly different chemical additives was used to stabilize the mud used under high, medium and low hot rolling temperatures starting from conventional one to polymers, and secondly its interaction with base oil and lime. The results demonstrate that the ester-based mud using our 2-EH ester is stable up to 400°F (204°C) with improved rheology and acceptable amount of filtrate volume as shown in sample 23. All filtrate amount was measured and multiplied by 2 referring to the difference in filtration area of high and low pressure cells, 45.8 cm², 22.9 cm² respectively.

Biobased Lubricants: Harnessing the Richness of Agriculture Resources

Table 13 Ester based mud formulations with conventional type of additives

Materials	1/12ppg,250F	2/12ppg,250F	3/12ppg,250F	4/12ppg,250F	5/12ppg,250F
2-EH C12 E	0	0	0	193.17	190.557
C12 ME	207.696	205.84	204.45	0	0
Confi mul p	3	4	4	4	4
Confi mul s	6	6	6	6	6
Confi mul ht	0	0	0	0	0
Confi mul xht	0	0	0	0	0
Confi gel	0	0	0	0	0
Confi gel ht	1	1.3	1.3	1	1
Confi gel xht	0	0	0	0	0
Confi trol	0	0	0	0	0
Confi trol ht	4	6	8	8	12
Confi trol Xht	0	0	0	0	0
Lime	5	2	2	2	2
Drill water	14.95	40.59	40.31	39.92	39.377
Calcium chloride	14.84	14.71	14.6	14.46	14.267
Barite	201.72	203.77	203.53	215.66	214.99
Rev Dust	20	20	20	20	20

Rheology	Mud 1/250 F		Mud 2/250 F		Mud 3/250 F		Mud 4/250F		Mud 5/250F	
600 rpm	54	50	61	54	46	72	70	56	70	73
300 rpm	35	33	43	35	27	44	42	33	45	45
200 rpm	28	25	33	26	18	33	31	23	36	35
100 rpm	21	18	24	20	11	24	22	14	26	25
6 rpm	11	10	14	10	5	11	9	4	13	10
3 rpm	10	9	12	9	4	10	8	3	11	9
Pv, cP	19	17	18	19	19	28	28	23	25	28
Yp, lb/100 sq ft	16	16	25	16	8	16	14	10	20	17
Gel strength @ 10 sec	11	9	13	9	8	10	11	6	14	13
Gel strength @ 10 min	14	12	16	14	9	15	14	7	17	19
ES volt	1799	1689	1769	1549	887.3	625	1999	1999	1999	1999
HTHP filtrate, ml		60		20		2		40		2
Mud cake thickness, mm		8.5		7		2		15		1

Table 14 Ester based mud formulation with conventional and advance types of additives

MATERIAL	6	7	8	9	10	11	12	13	14	15
	300F	300F	300F	300F	300F	300F	300F	300F	300F	300F
2-EH C12 E	0	0	0	0	0	189.4	187.7	187.6	187.41	
C12 ME	204.05	199.384	197.62	196.773	191.49	0	0	0	0	0
Prim Emul 1	4	4	4	0	4	4	4	4	4	4
Sec Emul 1	6	6	6	1	8	6	8	8	8	8
Emul 2	0	0	0	10	0	0	0	0	0	0
Emul 3	0	0	0	0	0	0	0	0	0	0
Viscosifier 1	0	0	0	0	0	0	0	0	0	0
Viscosifier 2	1	1.25	1.5	1	1	1	1	1.25	2	2
Viscosifier 3	0	0	0	0	0	0	0	0	0	0
Fluid Loss agent 1	0	0	0	0	0	0	0	0	0	0
Fluid Loss agent 2	8	10	12	12	12	12	12	12	12	15
Fluid Loss agent 3	0	0	0	0	0	0	0	0	0	0
Lime	5	5	5	5	5	5	5	5	5	5
Cac12	40.23	40.676	40.316	40.144	39.067	39.1	38.8	38.8	38.7	38.519

	14.58	14.527	14.398	14.337	13.952	14	13.9	13.8	13.8	13.757											
WATER																					
BARITE	201.34	205.613	203.87	203.946	209.69	211.2	211.3	211.2	210.7	212.015											
Drill solid	20	20	20	20	20	20	20	20	20	20											
Rheology	300F		300F		300F		300F		300F		300F										
	B	A	B	A	B	A	B	A	B	A	B	A									
600 rpm	49	95	43	111	47	95	50	88	58	127	79	81	83	73	80	84	84	80	76	84	88
300 rpm	28	56	24	67	28	60	28	52	34	82	52	50	50	39	50	50	49	44	51	51	51
200 rpm	19	42	18	49	19	46	19	39	24	64	25	28	37	29	37	36	39	32	41	37	37
100 rpm	13	27	11	32	13	32	12	24	16	43	16	17	24	18	26	22	28	19	28	23	23
6 rpm	4	7	4	9	5	12	4	6	7	15	7	6	8	4	11	5	12	6	11	8	8
3 rpm	4	5	4	8	5	10	4	5	6	12	7	5	8	4	10	4	11	4	10	7	7
Pv	21	39	19	44	19	35	22	36	24	45	27	31	33	24	30	34	31	32	33	37	37
Yp	7	17	5	23	9	25	6	16	10	37	27	19	17	15	20	16	18	12	18	14	14
Gel 10'	7	9	7	12	9	13	7	7	13	15	10	14	10	5	13	7	14	7	12	7	7
Gel 10''	8	15	8	16	11	14	8	7	17	17	13	17	15	7	17	10	18	10	19	12	12
ES volt	1967	1634	1971	1753	1909	1889	1989	1653	1621	1989	1681	1899	1789	1534	1685	1300	978	1611	1985	1539	1539
HTHP filtrate	60			50	45			50		35			20		10		10			2	2
Mud cake thickness mm						8		8.2		8		8	6		5		5		5		1.5

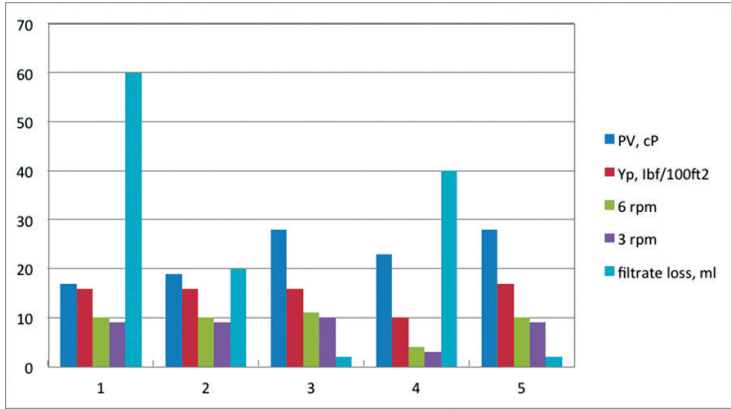


Figure 17 Comparison between C12 ME and 2-EH C12 ester @ 250F

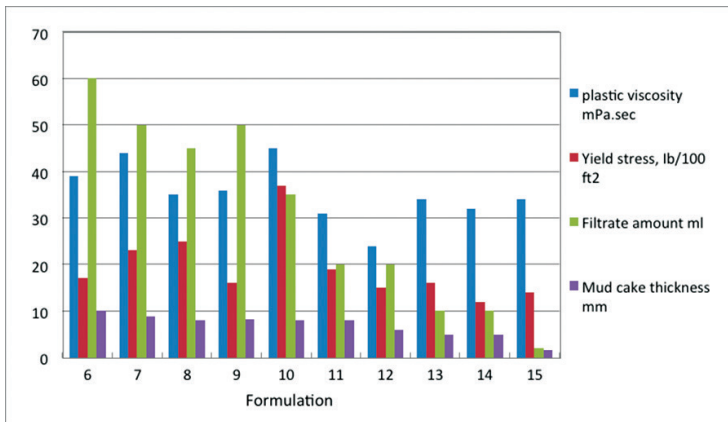


Figure 18 Comparison between C12 ME & 2-EHC12 E @300 F and 100 Psi

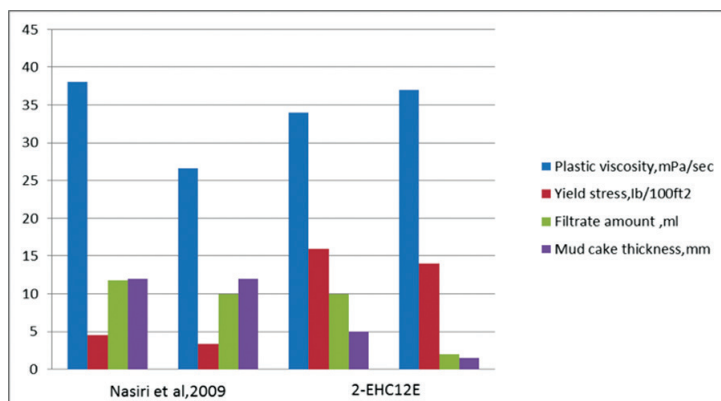


Figure 19 Comparison between Nasiri *et al.*, 2009 ester based mud and 2-EHC12 E based mud @300 F

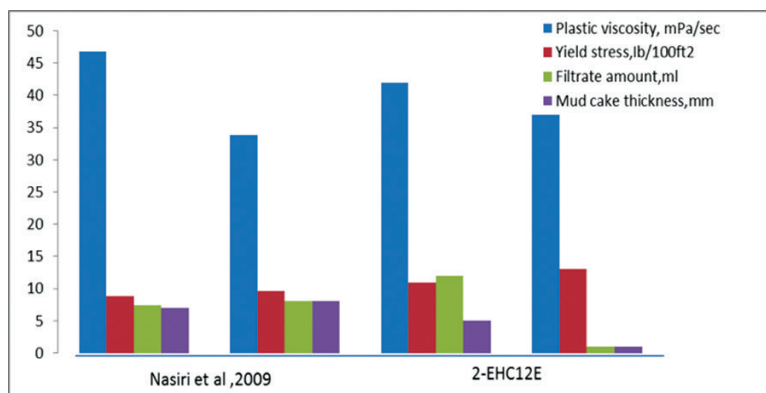


Figure 20 Comparison between Nasiri *et al.*, 2009 ester based mud and 2-EHC12 E based mud @350F

Table 15 Ester based drilling mud with advanced and ultra- advanced additives

MATERIAL	16 350F	17 350F	18 350F	19 350F
2-EH C12 E	201.9	191.7	198.24	201.8
Emul2(primary&se condary)	12	10+2		10+2
Emul3(primary&se condary)	0	0	10+2	0
Viscosifier 2	0	1.3	0	0
Viscosifier 3	0.5	0	1	1.5
Loss agent 2	0	15	0	0
Loss agent 3	7	0	6	5
LIME	5	2	2	2
CALCIUMCHLORIDE	14.9	14.1	14.6	14.9
WATER	41.7	41.4	41	41.7
BARITE	208.6	210	216.4	211.9
Drilled solid	20	20	20	20

Rheology	16 350F		17 350F		18 350F		19 350F	
	B	A	B	A	B	A	B	A
600 rpm	79	164	52	95	66	87	54	84
300 rpm	42	95	27	53	38	50	30	52
200 rpm	30	69	19	39	27	37	21	40
100 rpm	18	42	12	23	17	24	13	27
6 rpm	4	9	3	5	6	8	3	9
3 rpm	2	7	3	5	4	7	3	8
Pv, cP	37	69	25	42	28	37	24	32
Yp, lb/100 sq ft	5	26	2	11	10	13	6	20
Gel strength @ 10 sec	6	7	6	5	6	8	4	9
Gel strength @10 min	9	10	7	5	9	10	6	11
ES volt	606	633.3	650	582	1080	607	718	638
HTHP filtrate, ml		20		12		1		12
Mud cake thickness, mm		8		5		1		5

Table 16 Ester based mud formulation with ultra-advance type of additives

MATERIAL	20 412F	21 412F	22 412F	23 412F
2-EH C12 E	201.9	198.2376044	194.41	193.9
Emul 2	12	0	0	0
Emul 3	0	12	12	12
Viscosifier 3	0.5	1.5	1.5	1
Fluid Loss agent 3	7	6	5	6
LIME	5	2	2	2
CALCIUM CLORIDE	14.9	14.629	14.35	14.6
WATER	41.7	40.963	40.17	41
BARITE	208.6	216.37	216.4	216.4
Drilled solid	20	20	20	20

Rheology	20		21		22		23	
	412F	412F	412F	412F	412F	412F	412F	
	B	A	B	A	B	A	B	A
600 rpm	79	165	77	115	64	93	66	95
300 rpm	42	94	45	66	35	52	38	53

200 rpm	30	69	29	48	25	37	27	38
100 rpm	18	44	18	28	16	23	17	23
6 rpm	4	9	6	6	6	7	6	9
3 rpm	2	7	5	5	5	5	4	8
Pv, cP	37	71	32	49	29	41	28	42
Yp, lb/100 sq ft	5	23	23	17	6	11	10	11
Gel strength @ 10 sec	6	7	8	7	9	7	6	7
Gstrength @ 10 min	9	10	17	9	16	9	9	9
ES volt	646	636.43	1134	678	1217	997	1116	989
HHPH filtrate, ml		20		10		7.5		10
Mud cake thickness, mm		8		8		4		6

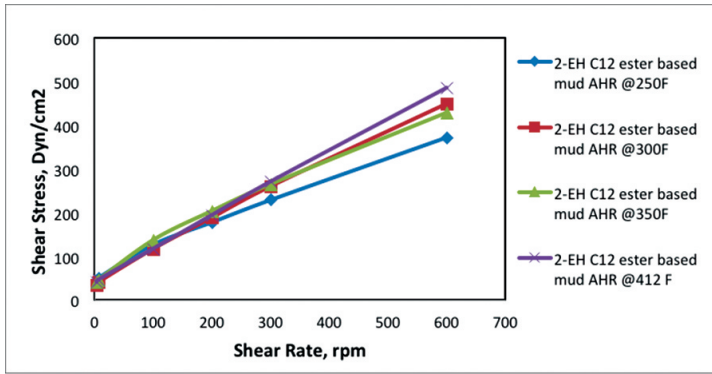


Figure 21 Rheology of 2-EH C12 ester based drilling fluids under different hot rolling temperature

GREEN TRANSFORMER OILS

Today, everywhere, electric power industry is managed systematically to ensure that an adequate supply of electricity is available to meet all demand requirements at any given instant. Transformers are keys to the transmission and distribution of electrical power, acting as “gearboxes” to ensure the right type of voltage reaches the private or industrial consumers. The transformers in electric power transmission and distribution systems are expected to provide reliable and efficient service for their life expectancy of at least forty years. The quality of the oil in a transformer plays a very important role in satisfactorily performing its functions. Mineral oil derived from petroleum crude, has been the main insulating liquid in industrial power systems since 1900s (Sierota and Rungis, 1995) because of its good ageing behavior, low viscosity, ready availability and low cost (Rouse, 1998). Polychlorinated biphenyl (PCB) based insulating liquids were introduced in early 1930s as the answer for problems related to the requirement for high fire security standard procedure. Until the 1960s PCB did not raise environmental concern

until 1970s when the public started to question the hazards they posed to the environment and human (ATSDR, 1990).

Driven by the desire for a safer non-flammables and environmentally acceptable insulating liquid for use in power equipment, researchers and engineers have investigated countless alternatives to mineral oil and significant advances have been achieved during the last four decades [Oommen, 2002; Clairborne and Pearce, 1989; Plessner and Reynolds, 1976; Senkevitch *et al.*, 1987). The aim of this work is to provide an overview of the main properties of alternative insulating liquids and to show their possibilities to replace mineral oil as we embark on the journey towards green transformer oils. Ultimately, local vegetable oil such as palm oil or its derivatives would be analysed and developed into alternative palm based transformer oil.

Synthetic Ester-Based Transformer Fluids

Esters are a broad class of organic compounds. They are available as natural agricultural products or chemically synthesized from organic precursors. These esters are broadly divided into two types, which are synthetic and natural. Synthetic esters have been investigated in Europe, North America, Russia and India and quiet and “extensive data of general and fluid specific” nature has been established. As can be seen from Table 17, there are many different specifications available for applications of liquid insulating oils. An example of thoroughly studied synthetic ester transformer oil is Midel 7131, developed by M & I Material Limited in the United Kingdom in 1978s based on chemistry of pentaerythritol tetra ester. In 1979, Ciba-Geigy introduced the first ester-based “less flammable” insulating fluid to replace; among other PCBs in electrical equipment (Boss and Phillips, 1998) Cooper Power System also produced Envirotemp 200.

Table 17 Specifications for Transformer Oils

Fluid Types	Fluid Specification	
	IEC	ASTM
Mineral Oil	IEC 60296	D 3487
Recycled Mineral Oil	IEC 62701	N.A
Synthetic Ester	IEC 61099	WORK ON GOING
Natural Ester	IEC 62770	D 6871
Silicon Oil	IEC 60836	D 2225
Synthetic Aromatic Hydrocarbon	IEC 60867	N.A

Natural esters are now derived from native plants such as soybean, canola, jatropha, karanja, castor, palm, sunflowers, cottonseed, peanut, olive, coconut, corn and beech. Some of these products are now being used extensively to produce natural esters that are similar to synthetic esters such as polyol esters (Lewand, 2004). Examples of current commercially known natural ester dielectrics are shown in the Table 18.

Synthetic ester dielectric fluids, more commonly called polyol ester (POEs) because of their synthesis from a polyhydric alcohol and fatty acids have suitable dielectric properties and significantly more biodegradable than mineral oils or high molecular weight hydrocarbons. Their high cost compared to other less-flammable fluids generally limits their use to traction and mobile transformers and other specialty applications. An example of a commercially available polyol ester based insulating oil is made from a branched mono-acid (C_5 to C_{18}) and alcohol *pentaerythritol* or 2, 2-bis (hydroxymethyl) 1, 3-propanediol (IUPAC nomenclature).

Recently, new vegetable-based insulating oil for transformers, called palm fatty acid ester, has been proposed. Relative to mineral oil its dynamic viscosity is 60% lower and its relative permittivity is 30% higher (Kano *et al.*, 2008; Abdelmalik, 2011). Using chemical treatment of filtered samples, Abderrazzaq and Hijazi (2012) significantly improved the acidity of olive oil.

Table 18

Name	Type	Manufacturer
Biotemp	Comprised mostly of monounsaturated high oleic acid triglyceride vegetable oils. The oleic acid group is defined as having one carbon double bond, part of the 18 carbon atoms in the hydrocarbon chain of a carboxylic acid. Examples of high oleic oils are sunflower, safflower and rapeseed (canola).	ABB Inc
Biotrans	A mixture of partially hydrogenated soybean oil high in oleic acid content, methyl esters produced from soybeans, palm or coconut oils used to thin the dielectric liquid.	Cargill
Environtemp FR3	Edible seed oil based dielectric liquid. It is a natural ester (triglyceride fatty acid ester) containing a mixture of saturated and unsaturated fatty acids with 14 to 22 carbon length chain containing one to three double bonds. Suitable vegetable oils which may be used independently or combined include soya, sunflower, and rapeseed (canola)	Cooper Power System, now by Cargill

Neugen 1540 and Plus	Developed from blending of monounsaturated fatty acid containing oil with alkyl ester and antioxidant additive	Bioelectric, Australia
Nycodiel 1244 / 1255	Developed from renewable raw material and used as synthetic dielectric fluid	Nyco, France
PFAE	Developed from palm oil based fatty acid ester	Lion Corp, Japan
SunOhm Eco	Developed from fatty acid of canola oil	Kanden Engineering, Japan

Synthesis of Palm Oil-based Neopentyl Glycol Ester as Transformer Oil

The synthetic ester selected as the base oil in the formulation of the transformer oil is the palm oil-based neopentyl glycol ester. The synthesis of the ester was conducted using the low-pressure technology as described by Yunus *et al.*, 2003. The starting materials were high oleic palm-based methyl ester and neopentyl glycol. Response surface methodology (RSM) was used to determine the optimum conditions as shown in Figure 22 and 23. The optimized conditions for synthesis of NPG are 2:1.3 (POME:NPG), 182°C, 0.6 mbar and 1.18%, diester for molar ratio, temperature, pressure and catalyst concentration composition respectively. Catalyst concentration was found to be the most significant factor, followed by temperature and pressure. Second order models were obtained to predict the response analyzed as the function of the three variables and were found to describe the experimental ranges studied adequately.

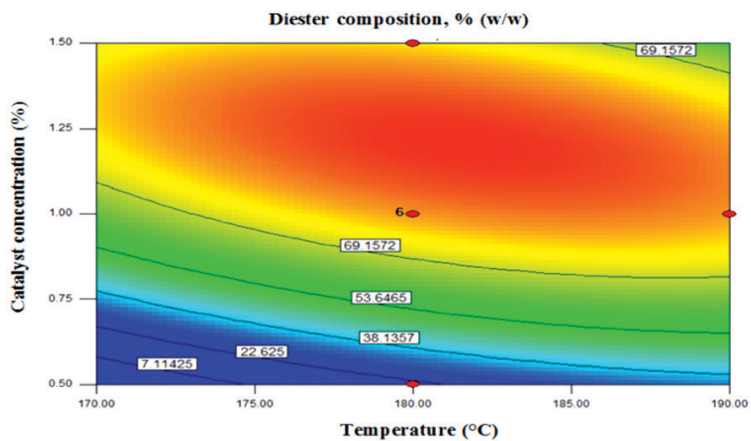


Figure 22 Effect of catalyst concentration and temperature on NPG diester composition

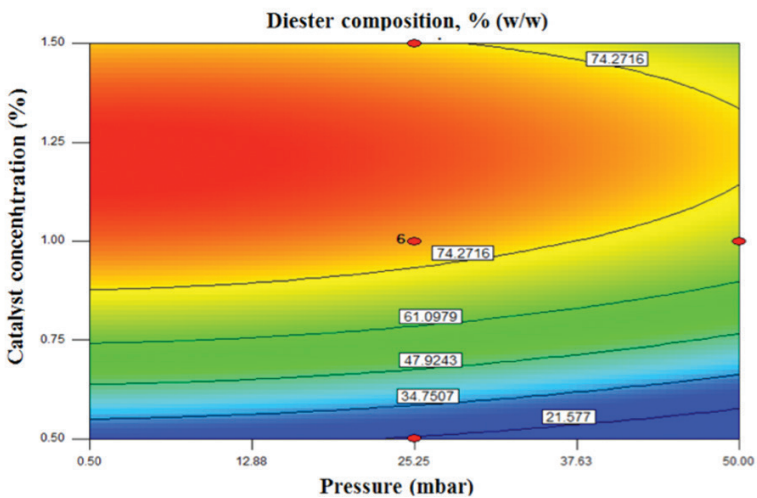


Figure 23 Effect of pressure and catalyst concentration on NPG diester composition

In conclusion, biodegradable synthetic and natural esters are good alternatives for mineral oils, especially in such situations when the power transformer has to be installed in the places for which the restricted environmental regulations are specified. Besides having excellent biodegradability, high flash point and good properties concerning the AC electrical strength, esters have also negative features, which should be taken into account in the design phase and during the exploitation of the transformer with esters. The parameters of the designed transformer must be based on the knowledge about these negative features. A designer should know that the esters are susceptible to the action of a concentrated heat flux, have the worse cooling properties than mineral oil, and lower lightning strength. The final product – power transformer filled by ester – will be in effect the more expensive device, but taking into consideration the pro-ecological tendencies reigned on the transformer market and still increasing for new environmentally friendly products, in the future the cost will likely be lower.

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BIOGRAPHY

ROBIAH BT. YUNUS was born on 20 October 1964 in Kota Bharu, Kelantan. She is the eldest in the family of seven siblings. His primary education began at SRK Kadok in 1971 and went for her secondary education at SMK Zainab, Kota Bharu, Kelantan from 1977 to 1979 and continued further at Sek Men Sains Tuanku Syed Putra, Perlis from 1980 to 1981.

In Feb. 1982, she was awarded a scholarship by PETRONAS to pursue her study in Chemical Engineering in USA. In 1986, she completed her degree of Bachelor of Science in Chemical Engineering from the University of Alabama USA with the CPA of 3.5/4.0 (top 5% in her class). Following her graduation, in November 1986, she joined the Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia (UTM) as an Assistant Lecturer. In July 1988, she obtained another scholarship from the Public Service Department, Malaysia to pursue her Master Degree at the University of Leeds, United Kingdom. She graduated with Masters of Science in Integrated Design in Chemical Plant in 1989 and was later promoted to a senior lecturer in 1995. At UTM, she lectured in various subjects related to chemical engineering field, including process control, thermodynamics, mass transfer, heat transfer, chemical process principles, unit operations and process and plant design.

In February 1997, Robiah joined the Department of Chemical and Environmental Engineering, Universiti Pertanian Malaysia (now known as Universiti Putra Malaysia, UPM). Since the chemical engineering program was recently set up, she helped to establish the infrastructure for the program. At UPM she also taught various subjects including thermodynamics, heat transfer, chemical process principles and process and plant design etc. In September 1999, she enrolled as a full-time PhD candidate in the Chemical Engineering

at UPM. Upon completing her PhD in December 2003, she was immediately appointed as Head of the Department of Chemical and Environmental Engineering in January 2004. In May 2004, she was promoted to an Associate Professor and later to a Full Professor in October 2010.

Robiah was the Head of Chemical and Environmental Engineering Dept., UPM from 2004 to 2008. During the 5 years of leading the department, she managed to obtain the international accreditation from the Institution of Chemical Engineers, UK for the Bachelor in Engineering (Chemical) program. The department also obtained RM12 million research grants and became the top engineering department in UPM. In 2009, she was appointed as Deputy Dean (Research and Postgraduate Studies). In early 2011, she was the Acting Dean for the faculty and later in 2011 as the Deputy Director of Institute of Advanced Technology (ITMA). She has been the Director of ITMA since May 2012. Since 2012, she has been leading the institute in managing research activities focusing on advanced materials and nanotechnology. Three key areas, which are represented by the three laboratories, have been established. The areas are materials synthesis and characterization, materials processing, and technology and functional devices. She has been at the forefront in realigning the institute to focus on its new niche areas, achieving 5-star performance and promoting interdisciplinary research in the material science and technology cluster.

At university level, she is the head of research cluster in Applied Science and Engineering. She plays leading roles in the grant evaluation exercises for various grants such as Putra, Sciencefund, FRGS, ERGS, PRGS, and LRGS grants. At national level, she has been assisting Ministry of Science, Technology and Innovation in evaluating grant applications for Sciencefund and Technofund

grants. She has also been invited to give talks by other universities on preparing proposals for research grants. She is also one of the accreditation panels for the Malaysian Qualification Agency (MQA). She is a member of IEM and Mytribos.

At international level, she is a fellow and chartered engineer of the Institution of Chemical Engineers, UK (IChemE). She is a member to Malaysian Professional Fellowship Forum who is given the authority by the IChemE, UK to evaluate applications and conduct interviews for chartered engineer candidates. She was invited as speaker and chair-session in various international conferences as well as to review articles for ISI journals such as Fuel, Bioresource technology etc. She won many awards at invention and international level research exhibitions including special awards. From INPEX, 2010 held in Pittsburgh, she won 3 awards; EUREKA, 2 awards; IENA, 1 award; British invention show, 2 awards; Geneva, 2 awards. She is also member of the American Society of Chemical Engineers and Society of Tribology and Lubrication Engineers (STLE).

She had supervised and co-supervised 38 PhD candidates, 45 MSc researches, and over 40 BS students. To date, 45 of her postgraduate students have graduated, 15 are PhD students. She was the main supervisor for 18 of these graduated students. She has published over 200 articles, of which 105 are in reputable journals. She had published his work in Thomson ISI journals, including the flagship journals such as JAOCS, Fuel, Catalysis, Industrial Crops, Bioresource Technology, EIJST, etc. She also published 2 books from her students' thesis and 2 chapters in book.

She is very active in research primarily in the area of biobased products synthesis and technology development. She led numerous research projects worth more than RM15 million and authored about 110 publications in international reputable journals. Her active

and leading involvement in research has resulted in development of 2 patents and 6 pending patents that are (i) “Synthesis of Trimethylolpropane Esters as Lubricant Base Stock”, Malaysian Patent Registration Number: MY-140833-A (ii) “Integrated Method For Producing Biodiesel Fuel From Crude *Jatropha Curcas*” PI 20093286 (iii) “A Method for producing polymer-encapsulated nanoparticles, Application Number: PI 2011003395 (iv) “Coagulant Agent for Water Treatment, PI 2011700007 (v) “Method for Producing High Purity Graphitic Carbon Nanostructures, PI number: PI 2010003360 (vi) “*Jatropha Curcas* L. Fruit Shelling Machine, PI number: PI 2010002417 (vii) “Light Weight Exterior Body parts for Vehicle and Composite Used Thereof”, PI number: PI20070745 (viii) “Therapeutic Agent for Treating Cancer; Inventor’ PI number: PI20072475.

She made a major discovery in her first patent where she discovered the use of low-pressure technology that enable the yield of lubricant base oil to increase significant within fraction of time. In addition, the palm-based lubricant exhibits low pour point of -32 degree C and high thermal stability, which have been identified as major impediment in palm oil utilization as lubricant base oil. Since then, she has been developing different kinds of esters as lubricant base oils for various applications. Hydraulic fluid, metal working fluid, tapping oil, oven chain oil and drilling fluid are among the biolubricants that are currently being developed for commercial purposes. Ester-based oil drilling fluid has also been developed using the low-pressure technology. The ester-based mud is superior and the production cost is much lower due to the efficient technology. The ester-based mud enhanced with graphene has good potential to replace conventional OBM for high temperature application above 450°C . Green transformer oil is also being developed driven by the desire for a safer, non-flammables and environmentally

acceptable insulating liquid for use in power equipment. Two of these products are developed jointly with interested companies. She has also successfully completed two contract research projects with Petronas Chemicals Group and Puncak Niaga totalling almost RM1 million. She is currently pursuing a research collaboration with Scomi Oils Tools in developing green drilling fluid. Scomi is the world leader in supplying drilling fluid to various international oil and gas companies.

Currently, she is leading a national long-term research (LRGS) program on Palm Oil Milling worth RM5.855 million. There are a total of 50 researchers from 5 universities involved in the program. This program aims to enhance the productivity and sustainability of the Malaysian palm oil milling industry by improving the existing milling technologies and increasing biomass utilization. Specifically, the program is to elucidate the fundamentals issues in the existing milling technology for possibility of improving oil extraction rate (OER) by reducing oil losses in palm oil mill, to study novel materials and technologies in monitoring and reduction of FFA in palm oil condensate, to examine the impacts of locally produced effective microbes (EM) on the properties of EFB composts to improve biomass utilization, to elucidate the physico-chemical properties of press cake for opportunity to improve pressing technology, and enable the use of green technology (solvent-free process) to recover oil and kernel losses in the press cake, to improve fruit grading schemes by developing sensors based on microwave and dielectric properties for quick and accurate determination of the quality of FFB at palm oil mills, to identify and characterize the wastewater from palm oil mill for opportunity to develop new treatment technology towards zero water discharge and finally to determine the economic and financial feasibility of the new technologies in Malaysian palm oil milling industry. Presently

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Dolphins (M) Berhad has commercialized one of the projects on the high pressure sterilization and they are considering a few more from this program.

ACKNOWLEDGEMENT

I am most grateful to Allah SWT for His blessings and guidance, I have reached this important milestone of my life.

Firstly, I would like to express my gratitude to all my colleagues and staff in the Department of Chemical and Environmental Engineering, Faculty of Engineering and the Institute of Advanced Technology, UPM. My heartfelt gratitude to the following individuals who have inspired me throughout my career, Allahyarham Dato' Ir. Dr. Radin Umar Radin Sohadi, Prof. Dato' Ir. Dr. Mohd Saleh Jaafar, Prof. Datin Paduka Dr. Aini Ideris and Prof. Dato' Abang Abdullah Abang Ali.

My special appreciation and thanks also go to all my dedicated postgraduate students and research fellow, Dr Umer, Dr Chong, Dr Azhari, Dr Shanti, Dr Ferra, Dr Herliati, Dr Nasrin, Zubaidah, Anita, Sarina, Liza, Hamidah, Mahshid, Fateme, Chang, May, Zaini, Saiful, Kiwi, Atiqah, Liyana, Ummi, Ali, Ferial, Lina, Mimi, Farah, Yayat, Soheil, Hadi, Ummi Hasanah, Dalila, and Aznizan as well as other individuals who rendered me support and assistance in pursuing my research interest in the area of biobased chemicals.

I also gratefully acknowledge Universiti Putra Malaysia, Ministry of Science, Technology and Ministry of Higher Education for their financial support.

I am indebted to my late parents Yunus bin Yusuf and Khadijah Haji Awang for their doa, love, support and encouragement in the early part of my career.

Last but not least, my special thanks to all my family members - my beloved husband, Salahuddin Abdul Manap, sons – Mohd Muzammil and Mohd Mudzakhir, daughters Nazratul Fareha, Aina Nadhirah, and Nina Fatma, grandson, Daniel Mikhael for their love, endless support and understanding. Thank you and may Allah SWT bless all of you.



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