TRIBOLOGICAL PERFORMANCE OF PALM OIL-BASED LUBRICANT WITH NANOPARTICLES ADDITIVE

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ABSTRACT

Lubrication is an essential tool in human life. As the technology advances, the method of lubrication becoming a lot complex and we relied heavily on mineral oil or synthetic oil which are harmful for the environment. Researchers around the world have started to shift their focus on bio-lubrication that is more environmentally friendly. Bio-lubricant based on palm oil could be one of the best replacements of standard lubricant. With nanoparticle additives, the tribological performance of the bio-based lubricant could be improved even more. This investigation will be centred around the tribological characteristic of bio based trimethylolpropane (TMP) ester with nanoparticle and nanocomposite additive. Additives that in focus are Copper Oxide (CuO) and Titanium Dioxide (TiO_2). The nanocomposites are the mix of both nanoparticles with different configuration ratio. The aim of the investigation is to obtain the tribological performance of all the targeted samples and compare it to understand the best sample in term of tribology. It is found that the bio based TMP ester have tribological potential against the conventional PAO8. For nanoparticles, Copper Oxide shown that the concentration of 0.1 wt.% produced the best tribological performance against other tested concentration. Titanium Dioxide nanoparticle with concentration of 0.1 wt.% also produced the best tribological performance against other tested concentration. For nanocomposite, it found that the configuration ratio of 1 Copper Oxide to 2 Titanium Dioxide yields the best tribological performance against other tested configuration ratios.

ABSTRAK

Bahan pelinciran adalah sesuatu alat atau bahan yang sangat penting bagi kehidupan manusia. Semakin berkembangnya teknologi, maka teknik-teknik bagi pelinciran juga menjadi semakin kompleks. Kita juga sangat bergantung kepada bahan pelinciran berasaskan minyak mineral dan minyak sintetik yang merbahayakan alam sekitar. Para penyelidik di seluruh dunia sudah mula beralih kepada kajian mengenai bahan pelinciran bio iaitu bahan pelinciran yang berasaskan bahan-bahan mesra alam. Bahan pelinciran bio berasaskan kelapa sawit mempunyai potensi yang besar untuk menggantikan bahan pelincir konvensional. Dengan bahan tambah atau aditif daripada partikel nano, prestasi pelinciran bagi pelincir berasakan bio dapat lebih lagi dipertingkatkan. Kajian ini akan berkisar mengenai ciri-ciri prestasi tribologi bagi bahan pelincir bio Trimetilolpropana (TMP) dengan aditif partikel nano dan komposit nano. Aditif yang berada di dalam kajian adalah kuprum oksida (CuO) dan Titanium dioksida (TiO_2). Komposit nano pula adalah compuran kedua-dua partikel nano tersebut dengan nisbah konfigurasi tertentu. Tujuan kajian ini adalah untuk mendapatkan data bagi sekaligus memahami ciri-ciri tribologi bagi sampel-sampel yang dikaji. Didapati bahawa pelincir berasakan bio TMP mempunyai potensi apabila dibandingkan dengan minyak konvensional PAO8. Untuk kajian partikel nano, CuO dengan kepekatan 0.1 wt.% mempunyai ciri-ciri tribologi yang terbaik berbanding sampel CuO dengan kepekatan yang lain. Dapatan yang sama juga ditunjukkan oleh sampel partikel nano TiO_2. Untuk komposit nano, nisbah konfigurasi 1 CuO terhadap 2 TiO_2 didapati mempunyai ciri-ciri tribologi yang terbaik berbanding nisbah konfigurasi lain yang diuji.

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TAN	Total Acid Number
TBN	Total Base Number
CuO	Copper Oxide
TiO_2	Titanium Dioxide
COF	Coefficient of friction
TMP	Trimethylolpropane
API	American Petroleum Institute
CO_2	Carbon Dioxide
PMA	Polymethacrylate viscosity modifiers
PPD	Pour Point Depressants
OCP	Olefin copolymer
VI	Viscosity Index
PAO	Polyalphaolefin
PPG	Polypropylene Glycol
FM	Friction Modifier
AW	Anti Wear
ZDDP	Zinc Dithiophosphates
HP	Hindered phenolic
EP	Extreme Pressure
TMDCs	Transition Metal Dichalcogenides
SEM	Scanning Electron Microscopy
ASTM	American Society of Testing and Materials
AISI	American Iron and Steel Institute

CHAPTER 1: INTRODUCTION

Fossil fuel have been one of the most important substance for human being since its inception. It provides us the electricity to light up our nights, energy for us to move from point A to point B, fire for us to make food and other bi-products of it have been beneficial for us. As more and more fossil fuel based products introduced, normally more demand will follows on. And in order to satisfy the consumer's demand, more fossil fuels will be extracted and used. It takes millions of years of natural phenomenon to create fossil fuels from remains of prehistoric plants and animals. Since it is widely produced and used, the price of fossil fuels currently is relatively low. However, since the source are limited and the usage are unlimited, fossil fuels reserve is said to be depleting (Barreto, 2018). In 2017 alone, 70% or world energy demand are fulfilled by oil and fossil fuels. For power generation and transportation, most of it rely on the combustion of fossil fuels. This combustion releases carbon dioxide and contribute to the greenhouse effect which results in global warming. Other acidic gasses from the combustion leads to a more acidic environment thus bring more harm to humans and other living organisms. The problem facing us includes increase energy demand, limited resources of fossil fuels and environmental damages from the usage of fossil fuels lead us to seek for alternative and sustainable sources to replace the fossil fuel-based product. (Mohanty, Misra, Drzal, & Environment, 2002).

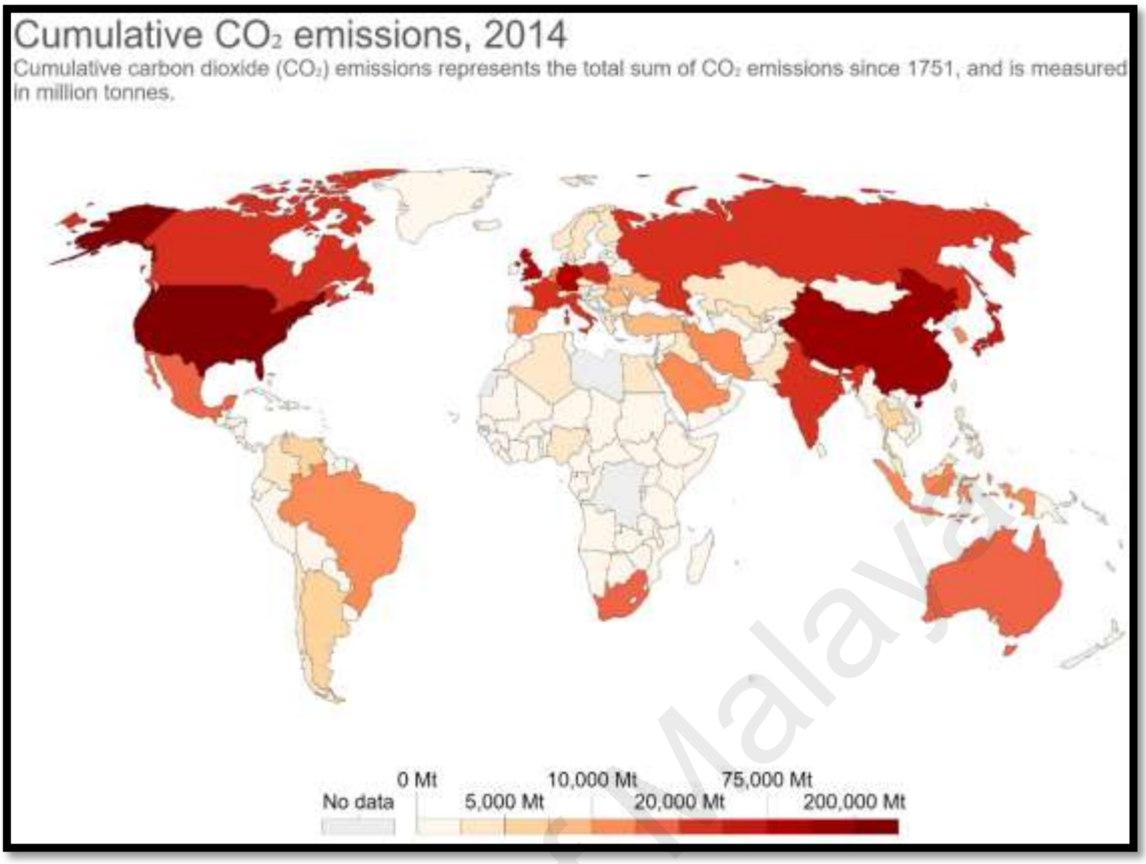

Figure 1: Worldwide cumulative carbon dioxide emission since 1751 until 2014.

One of widely used products of fossil fuel is lubricant. A lubricant is a substance that introduced between two parts or moving surfaces to reduce friction, heat and wear. Friction is resistance of one surface when moving over another surface. And it is one of the most important factors that targeted to reduce by applying lubrication. In an internal combustion engine application, it is estimated that 33% of energy losses comes from friction losses (Holmberg et al., 2012). Reducing the friction will results in a more efficient energy usage. Fossil fuel based lubricant including mineral oils and synthetic oils are widely used for lubrication as it is proven to have a wide range of viscosity thus compatible with most of desired applications. Since this type of lubricant comes from petroleum, there are growing concern of the very wide usage of it. This concern translate into increase interest in bio-based lubricant. Bio-based lubricant is lubricant that is obtained from living organisms including plant and animals. This type of lubricant is biodegradable and the waste of it is environmentally friendly and possess low ecotoxicity (Schneider & Agriculture, 2006).

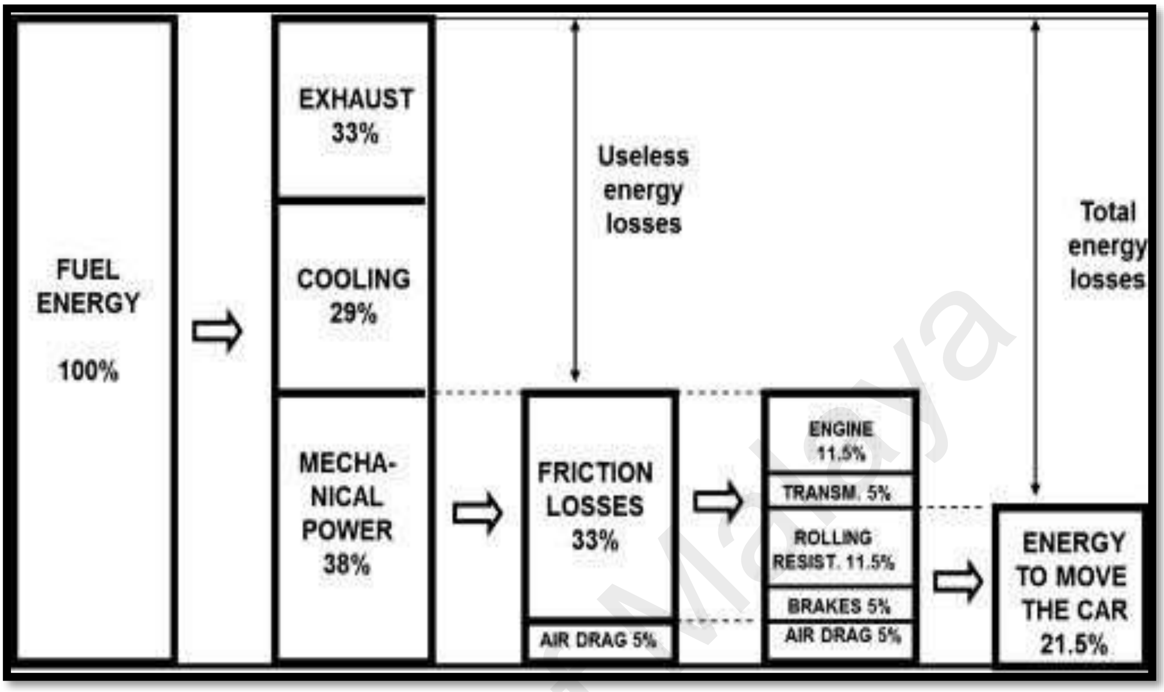

Figure 2:Frictional loss in internal combustion engine (Holmberg et al., 2012).

Studies have been conducted using different vegetable oil as base oil instead of mineral oil for lubricant. Formulated vegetable oil lubrication display better performance of coefficient of friction, good pitting resistance and similar scuffing load capacity to mineral oil, nevertheless lesser thermal and oxidative stability so at supreme loads vegetable oil-based lubricant turn out to be incompetent (Arnsek, Vizintin, & Technology, 2001; Barišić, Picek, & Oronite, 2003; Fox & Stachowiak, 2007). Compared to mineral based lubricant, bio-based lubricant has superior lubricity without any additives. This somehow show that bio-based lubricant has better prospect and properties compared to mineral-based lubricant. Lubricant are mainly composed of natural or mineral oil and partially impure. The deliberately chemicals impurity added improve overall performance of the lubricant. Due to reaction with metallic machinery parts and with the environment, additive present in the oil will deteriorate during operation. Normally, lubricant are composed of 95% base oil and 5% additives including solvent (Stachowiak & Batchelor, 2013)

1.1 Problem Statement

Lubricant is required to provide longer lifetime to machine, withstand higher temperature and pressure and enhancing energy efficiency. For many years mineral-based lubricant and synthetic-based lubricant had been are widely used in automotive and industrial sectors where consumers had gain trust to their functions and efficiency. Due to ecological imbalance, bio-based lubricant had been developed to substitute the conventional mineral based lubricant.

Bio-based lubricant is showing a positive outcome so far for its properties. However, there are still a lot of improvement possible to be done to further improve the tribological behaviours of bio-based lubricant especially in term of anti-wear and friction reducer agent. There are still many ongoing researches on bio-based lubricant to develop a better version of it.

Introductions of different type of nanoparticle additive such as copper oxide (CuO) and Zinc oxide (ZnO) to lubricant to strengthen its properties. Unfortunately, there are still massive numbers of studies needed to be carried out so that bio-based lubricant can be as good as mineral-based oil. Nanocomposite is the combination of two or more nanoparticles. This study is conduct to study the synergy between using a two-dimensional to two-dimensional nanocomposites and a two-dimensional to three-dimensional nanocomposite in its tribological behaviour.

1.2 Background Research

Lubricant with the best formulation can help reduce friction and heat lost. In industry with heavy machinery and automotive, the best lubricant can enhance the performance of the system, have longer service life and save cost. The mineral-based lubricant is been commercially used for the past decades. Now people start to realize the negative or bad effects of mineral-based lubricant to the environment. Furthermore, petroleum source takes millions of years to regenerate once it is harvested therefore it is said that it has finite source. Without further actions and improvement taken, there will come a day where we will be running out of petroleum. Besides, the used petroleum products have no proper decompose system so it harms the ecosystem. Many researchers start to find alternative to substitute many petroleum-based products due to the negative impacts. There are many studies conducted to enhance the performance of bio-based lubricant so that it can replace the consumption of mineral-based lubricant. It is said that bio-based lubricant has outperform the efficiency of petroleum-based lubricant with the significant additives. Researchers stated that bio-based lubricant that is vegetable oil possess excellent tribological properties and more environmentally friendly. However pure vegetable-based lubricant has low oxidative stability causing them to oxidize rapidly as temperature change is the major drawback of this oil. Additives are introduce to the base oil to give greater tribological property to the oil. Nanotechnology field have been explored to enhance performance of the bio-based lubricant. Nanoparticle additives have tremendous advantages in enhancing the properties of lubricants due to their nano scale molecules size. Some of the advantages is insoluble to non-polar base oil, less reactivity to other additives, better chances of film formation on different surfaces type, high durability and high non-volatility to withstand high temperature (Gulzar et al., 2015). Since nanoparticle possess good performance individually, it is possible for them to perform best as nanocomposites. Introduction of nanocomposites additives in bio-based lubricant is expected to have better performance that the commercial petroleum-based lubricants.

1.3 Objectives

I. To analyse the tribological behaviour of bio based TMP ester as a lubricant in comparison with commercial synthetic base oil.

II. To find the optimal nanoparticle additives concentration in bio-based lubricant.

III. To the investigate tribological improvement by using nanocomposite as bio-based lubricant additive.

1.4 Scope of Research

This project was conducted to enhance the performance of bio-based lubricant using nano additives. Trimethyl propane (TMP) which is the chemically modified vegetable oil show great potential to substitute the common petroleum-based lubricant with the right nanoparticle additives. Many studies have been conducted that prove that nanoparticle contribute good impact on the lubricant performance. Titanium Dioxide (TiO_2) and Copper Oxide (CuO) nanoparticle was chosen as nanoparticle to improve friction and wear performance of biobased lubricant. Based on the performance of individual nanoparticle, it is possible to further improve it by using a nanocomposite between the three nanoparticles. Using the optimum concentration of the nanoparticle obtained from the results, tribological behaviour of nanocomposite TiO_2/CuO are tested as lubricant additives with different configuration ratio. This research is conducted to study the contribution of nanocomposites on the tribological performance and effectiveness of bio-based lubricant.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

In this chapter, lubrication is discussed in detail. Review papers, journal and research report on previous studies as well as important term definition are reviewed to have a better understanding on the topic and to improve our approach on the project.

2.2 Lubricant

Lubrication have been a vital key for human being long time ago. It was believed that the ancient Egyptian started using fluid to cool down their wheel cart and found that it also reduces friction of the wheel cart. In modern days, lubrication becoming more advance as the invention of motorcars and jet engine as both of the applications are considered as extreme and mass application.

By applying lubrication, a film boundary is created on the surface of any application that reduce friction between the surface with another surface. It is important that a lubricant is rightly chosen for the application in order to prevent or minimise heat, friction, rust and corrosion. Important properties to be considered when choosing a right lubricant for an application will be as follows.

2.2.1 Viscosity

Viscosity is the main factor on choosing the right lubricant for any application. Viscosity is said to be the measurement of the fluid thickness under a certain condition. A higher viscosity means than the lubricant is thicker and stickier due to higher intermolecular friction. The chemical structure of an oil such as carbon chain length and degree of unsaturation effects the viscosity of the oil. A higher hydrocarbon length results in higher viscosity. Table below shows the viscosity commonly used vegetable oils.

2.2.2 Viscosity Index

Viscosity Index is an empirically derived, dimensionless number and it is a measure of change of viscosity with temperature. A lubricant will be affected by the temperature the most as the VI number decrease. On most application, lubricant with higher VI will be preferred as it have viscosity stability across wide range of temperature.

2.2.3 Flash Point, Fire Point and Pour Point

Flash point is the lowest temperature where vapor is produced by continuous heating of the lubricant. Fire Point is the lowest temperature where continuous ignition could be happened. From this explanation, flash point will be lower than the fire point. In order to have a good lubricant selection, the lubricant need to have higher Fire Point than the operational temperature of the application.

Pour point is the lowest temperature where the oil have the capability of flowing. Wax will be produced and solidify at the temperature lower than the pour point. For application on countries with four seasons, pour point will be one of the important aspect of lubricant selection. In crude oil. paraffin content in an oil is said to affect its pour point where higher pour point is associated with higher paraffin content in the oil (Mathews, Hatcher, Eser, Walsh, & Scaroni, 1998). The pour point for vegetable oils of various type are compiled by Gulzar (2018) as in the table below.

Table 1: Compilation of the physical characteristics for multiple kind of vegetable oils (Gulzar, 2018).

Vegetable Oil	Viscosity at 40 ^{O}C (cSt)	Density (g/cm$_3$)	Flash Point (^{O}C)	Pour Point (^{O}C)
Sunflower (Abolle, Kouakou, & Planche, 2009)	31.3	0.920	315	–12
Rapeseed (X. Wu, Zhang, Yang, Chen, & Wang, 2000)	34.75	0.917	323	–15
Soybean (Honary, 1996)	29.0	0.913	328	–10
Coconut (P. J. Singh, Khurma, & Singh, 2010)	28.05	0.926	228	–
Palm (Barnwal & Sharma, 2005)	39.6	0.918	267	–
Jatropha (Mofijur et al., 2012)	35.4	0.918	186	15
Castor (Scholz & da Silva, 2008)	260	0.95	229	–15

2.2.4 Oxidation Stability

Oxidation is chemical reaction that occurs between an element with oxygen and usually produced oxide of the elements. Vegetable oil often associated with lower oxidation stability than conventional synthetics oil of fully saturated such as PAO, synthetic esters, etc. The lower oxidation stability is associated with the presence of fatty acid in vegetable oils. The rate of oxidation related with the unsaturation of the chain of fatty acyl as shown in figure below.

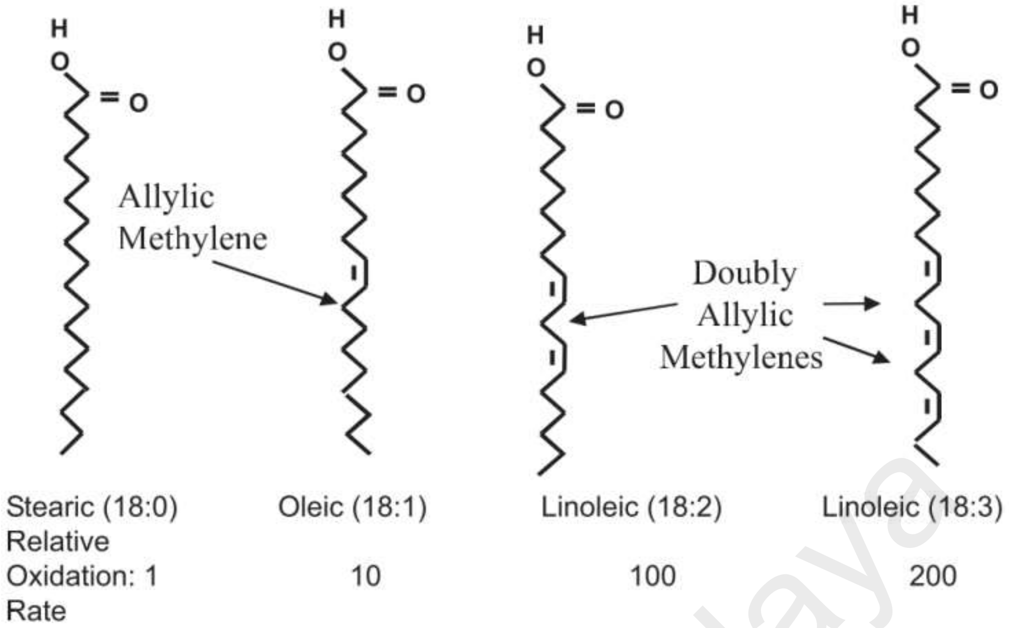

Figure 3: Approximation of the fatty acids rates of oxidation (Kodali, 2002).

Because of the reduced oxidation stability, vegetable oils will degradation will be faster than the mineral oils. This also results in higher dose of antioxidants than could be needed by vegetable oils to have a similar oxidation performance.

2.1 Lubricant Categories

There are three lubricant categories which often classified with. These are mineral oils, natural oils and synthetic oils. Mineral oils are mostly made of petroleum and it is one of the most common lubricant. Natural oils is oils that derived from plant or animal-based fats. Synthetic oils is a lubricant that consists chemical compound that is produced artificially. A few examples of synthetic oils are polyalphaolefins (PAOs), synthetic esters, polyalkylene glycols (PAGs), alkylated aromatics, perfluoroalkylpolyethers (PFPEs), etc.

2.2 Conventional Engine Lubricants

Lubricants that being widely currently used consists of hydrocarbons and induced with additives. Conventional engine oil usually made of hydrocarbon base (75 – 83 wt.%), viscosity modifier (5 – 8 wt.%) and other additives (12 – 18 wt.%). The common additives that are found in the conventional oil usually made of sulphur and phosphorus that is environmentally dangerous (Z. Li, Li, Zhang, Ren, & Zhao, 2014; Zhang et al., 2015). Conventional lubricant also believed to cause health risks such as irritation to the eye, dermatitis allergic and mutagenicity (Isaksson, Frick, Gruvberger, Pontén, & Bruze, 2002; Jaiswal, Rastogi, Kumar, Singh, & Mandal, 2014). The slow degradation as well as the high toxicity of the waste from the conventional lubricant are also considered as environmentally dangerous. From all the lubricant waste that entered the environment, 95% of them unsustainable to the environment (Schneider, 2006).

2.3 Bio-based Lubricants

Bio-based lubricants is said to be lubricants that is based on bio-based raw materials such as plant oils, animal fats or environmentally friendly hydrocarbon. These type of lubricants are biodegradable and non-toxic. Reeves (2013) estimate that 90% of all petroleum-based lubricants have potential to be replaced by bio-based lubricants. Researchers have been trying to find a suitable bio-based lubricants for wide applications such as greases (Dwivedi & Sapre, 2002), lubrication for engines (Mannekote & Kailas, 2011), lubrication for high speed rotation application (Battersby, Pack, & Watkinson, 1992; Randles, 1992), (Beitelman, 1998) and fluid for hydraulic application (Bartz, 2000; Kassfeldt & Dave, 1997).

Table 2: Examples of the producers of bio-based lubricants and their commercial names (Gulzar, 2018).

Company	Bio-based lubricant Commercial Name	Manufacturing Region	Applications
Fuchs	Locolub eco	USA/Europe	Greases, hydraulic fluids, gear oil and chain oils
Mobil	Mobil EAL	USA/Europe	Greases, hydraulic fluids and refrigeration oil
Shell	Ecolube	USA	Hydraulic fluids
Houghton Plc.	Cosmolubric	UK	Hydraulic oil
Aztec Oils	Biohyd & Biochain	UK	Hydraulic and chainsaw oil
Raisio Chemical	Raisio Biosafe	-	Hydraulic fluids, bar and chain oils
International Lubricants Inc	Lubegard	USA/Europe	Hydraulic fluids, gear oil and metalworking oils.
Karlshamns Binol AB	Binol	USA/Europe	Hydraulic fluids, metalworking oils, bar and chain oils
Bioblend Lubricants International	Bioblend	USA/Europe	Greases, hydraulic fluids, gear oil, bar and chain oils
Karlshamns Binol AB	Binol	USA/Europe	Hydraulic fluids, metalworking oils, bar and chain oils
Renewable Lubricants	Biogrease/oil	USA	Greases, hydraulic fluids, cutting oil, transmission oil, gear oil, metalworking oils, bar and chain oils, turbine drip oil, vacuum pump oil and crankcase oils.
Chevron Texaco	Biostar (Rando)	USA/Belgium	Hydraulic fluids
Environmental Lubricants	SoyTrak, SoyEasy	USA	Greases, hydraulic fluids, cutting oil, gear oil, metalworking oils, bar and chain oils

Manufacturing Inc.			
Moton Chemicals	Biolube	Europe	Greases, turbine drip oil, bar and chain oils.
Cargill Industrial Oils & Lubricants	Novus	USA/Europe /Japan	Hydraulic fluids, cutting oil, gear oil, metalworking oils, bar and chain oils

2.4 Palm Oil as bio-based lubricants

Palm Oil have a high potential to be used as the lubrication for various types of applications. This is due to the fact that palm oil fulfilled the criteria outlined by Rudnick (2013) for suitable bio-based lubricants which are:

1. Bio-based resources for oil production should be enough in quantity.
2. Bio-based oils should have more mono-unsaturated fatty acid than polyunsaturated fatty acids.
3. The bio-based resources should have a stable trading price.

Palm oil also found to have a high TAG content which is said to be the natural long-chain fatty acid tri-esters of glycerol that have a structure that are very similar structure to the petroleum base oils.

Table 3: Common vegetable oils average TAG content (Gulzar, 2018).

Plant	(% dry weight)
Corn	07
Sunflower	55
Castor	45

Rapeseed	40
Soybean	20
Palm Kernel	50

Also, since palm oil yield a larger oil content than other natural oils, uses of palm oil for lubrication in mass market could be archived with less land usage compared to other natural oils.

Since Malaysia is one of the major player in the palm oil market, tapping on the potential of palm oil for lubrication could be essential in keeping the country economic performance.

Table 4: Worldwide palm oil production by major producing countries. (USDA Economics, 2017)

Production (Thousand Metric Tons)	Year				
Country	2012-13	2013-14	2014-15	2015-16	(Aug) 2016-17
Indonesia	28500	30500	33000	32000	35000
Malaysia	19321	20161	19879	18250	21000
Thailand	2135	2000	2068	2100	2300
Colombia	974	1041	1110	1273	1280
Nigeria	970	970	970	970	970
Others	4478	4670	4614	4809	4945
Total	56378	59342	61641	59402	65495

2.5 Lubricant Additives

Chemical additives are additional substance that being added into a lubricant to enhance or improve performance of a lubricant. Such improvement that are target for lubricant are improved oxidation stability, reduced friction and wear effect, biological degradation stability and reduction in corrosion. Timeline below complied by Spikes (2015) shows the introductory year for some types of lubricant and table below complied by Shahnazar et al (2016) list additive types that their role in improving the performance of a lubricant.

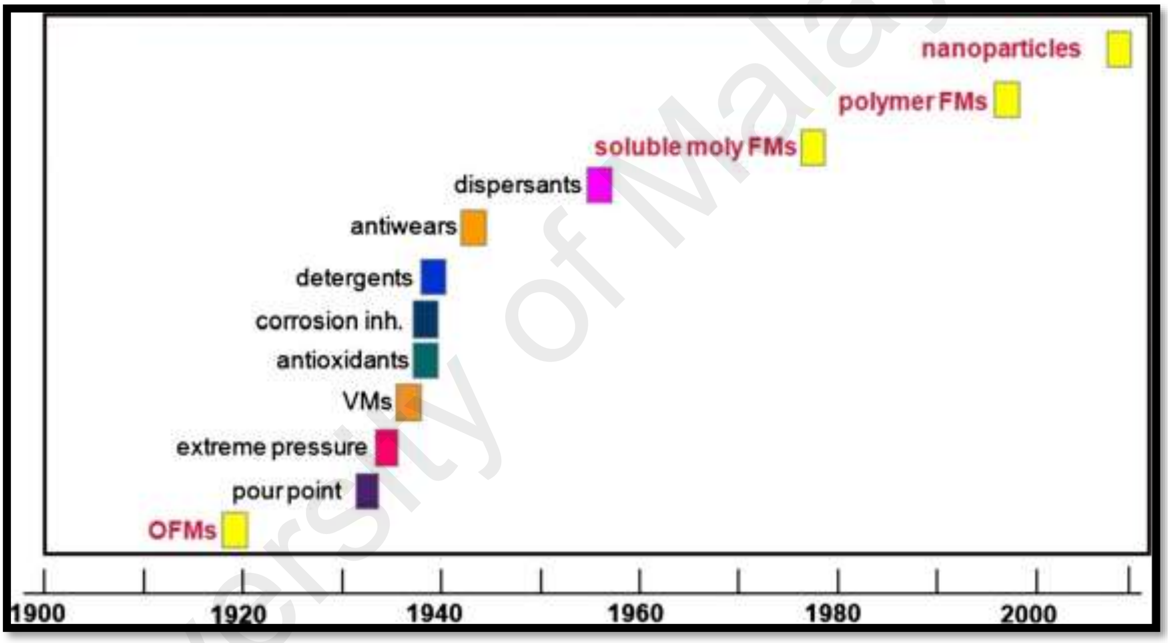

Figure 4: Timeline of lubricant additive introduction and development (Spikes, 2015).

Table 5: Common lubricant additives (Shahnazar et al., 2016).

	Additives	Effect
Deposit control additives	Anti oxidizing agent	Inhibit formation of corrosive component thru oxidative prevention
	Zinc dithiophosphates (ZDDP)	Prevent oxidation and wear
	Phosphate ester, phosphites and phosphonates (detergents)	Formed thinner and smoother film that preserve the surface against wear
	Alkylphenols, carboxylic acids	The alkaline compound neutralize the acid that causes erosion on the surfaces.
	Dispersants	Keep the surface clean by suspending the insoluble particles and contaminants
Film-forming additives	Graphite, MoS2, Boron nitride	Function as solid lubricant that minimize friction
	Organic friction modifier (Amide, amines, imides)	Increase lubricity and energy efficiency by adjusting the friction
Wear reducing agent and extreme pressure additives	Sulfurized Isobutene, Sulfurized Esters, Sulfurized Fatty Oil	Additives with sulphur contain in their oxidation and a heteroatom that is oxygen

Viscosity modifier	Olefin copolymer	Good thickening efficiency and low cost
	Polymethacrylate and pour point depressant	Improve viscosity index by thickening the oil and control wax formation

2.5 Nanoparticles as lubricant additives

Nanoparticles is particles that have nanometer size and it is one of the newest type of lubricant additives (Shahnazar et al., 2016). Researchers around the world have been trying to gain tribological improvement by using nanoparticles. Other than reducing friction, nanoparticles have found to have anti-wear or friction modifier and surfactant characteristic (Ohmae, Martin, & Mori, 2005). Gulzar et al (2016) have compiled a table consisting of nanoparticles as lubricant additives with its respective concentration.

Table 6:Summary of nanoparticles role and optimum concentration on the respective lubricants (Gulzar et al, 2016).

PARTICLE	LUBRICANT	NANOPARTICLE ROLE	CONC. (WT%)	OPTIMUM CONC. (WT%)	REFERENCES
ZnO	Mineral, PAO, sunflower, soybean	Friction Modifier and Anti wear	0.5	0.5	(Alves, Barros, Trajano, Ribeiro, & Moura, 2013)
	60SN base oil	Friction Modifier and Anti wear	0.5	0.5	(Ran, Yu, & Zou, 2017)

CuO	Coconut oil	Friction Modifier and Anti wear	0.1–0.6	0.34	(Thottackkad, Perikinalil, Kumarapillai, & manufacturing, 2012)
	Chemically modified rapeseed oil	Friction Modifier and Anti wear	0.1, 0.5, 1	0.5	(Arumugam, Sriram, & Ellappan, 2014)
	Mineral based Multi grade engine oil	Friction Modifier and Anti wear	0.5, 1, 1.5	1.5	(Jatti, Singh, & Technology, 2015)
	SAE 75W-85	Friction Modifier, Anti wear and extreme pressure	0.5, 1.0, and 2.0	2	(Pena-Paras et al., 2015)
	PAO8	Friction Modifier, Anti wear and extreme pressure	0.5, 1.0, and 2.0	2	(Pena-Paras et al., 2015)
	Mineral, PAO, sunflower, soybean	Friction Modifier and Anti wear	0.5	0.5	(Alves et al., 2013)

MoS_2	Coconut oil	Friction Modifier and Anti wear	0.25, 0.5, 0.75, 1	0.53%	(Koshy, Rajendrakumar, & Thottackkad, 2015)
	Mineral oil	Friction Modifier and Anti wear	0.25, 0.5, 0.75, 1	0.58%	(Koshy et al., 2015)
	EOT5#	Friction Modifier, Anti wear and extreme pressure	0.2, 0.5, 0.7, and 1.0	1	(Xie, Jiang, He, Xia, & Pan, 2016)
	SE 15W-40	Friction Modifier, Anti wear and extreme pressure	0.1, 0.5, 1.0, 2.0, and 5.0	*1	(Wan, Jin, Sun, & Ding, 2014)
CuO, MoS_2	Palm TMP ester	Anti wear and extreme pressure	1	1	(Gulzar et al., 2015)
SiO_2	Liquid paraffin	Friction Modifier and Anti wear	0.0125, 0.025, 0.05,0.1, 0.2,0.5, 1, 2, 4	0.05–0.5 wt%	(Peng et al., 2010)
	EOT5#	Friction Modifier, Anti wear and extreme pressure	0.2, 0.5, 0.7, and 1.0	0.7	(Xie et al., 2016)

PbS	Liquid paraffin	Friction Modifier and Anti wear	0.05-0.2	0.2	(Chen, Liu, & Physics, 2006)
Fe_3O_4	#40 engine oil	Friction Modifier and Anti wear	0.5, 1.0, 1.5, 2.0	1.5	(Gao, Wang, Hu, Pan, & Xiang, 2013)
hairy silica	PAO100	Friction Modifier and Anti wear	0.5,1,2,4	1	(Sui, Song, Zhang, & Yang, 2015)
Cu	PAO6	Anti wear and extreme pressure	0.5,2	0.5	(Viesca, Battez, González, Chou, & Cabello, 2011)
Cu Carbon		Anti wear and extreme pressure	0.5,2	0.5	(Viesca et al., 2011)
Ni		Friction Modifier, Anti wear and extreme pressure	0.5, 1, and 2	0.5	(Chou et al., 2010)
ZrO_2, ZnO, CuO	PAO	Anti wear and extreme pressure	0.5, 1.0, and 2.0 %	0.5	(Battez et al., 2008)
Carbon nanoonions		Friction Modifier and Anti wear	0.1	0.1	(Joly-Pottuz, Vacher, Ohmae, Martin, & Epicier, 2008)

ZrO_2/SiO_2	20$^{\#}$ machine oil	Friction Modifier and Anti wear	0.05, 0.1, 0.3, 0.5, 0.75,1	0.1	(W. Li, Zheng, Cao, & Ma, 2011)
Al_2O_3/SiO_2		Friction Modifier and Anti wear	0.05, 0.1 0.5,1	0.5	(Jiao, Zheng, Wang, Guan, & Cao, 2011)
Al2O3		Friction Modifier and Anti wear	0.05, 0.1 0.5,1	0.1	(Luo, Wei, Huang, Huang, & Yang, 2014)
ZrO_2		Friction Modifier and Anti wear	0.1, 0.5, 1	0.5	(Ma, Zheng, Cao, & Guo, 2010)
TiO_2	Servo 4T Synth 10W30	Friction Modifier and Anti wear	0.3, 0.4, 0.5	0.3	(Laad & Jatti, 2016)
$ZnAl_2O_4$	Lubricating oil	Friction Modifier and Anti wear	0.05, 0.1, 0.5, 1	0.1	(Song et al., 2012)

Other various types of nanoparticles were also investigated by researchers around the world (Bakunin, Suslov, Kuzmina, & Parenago, 2005; Bakunin, Suslov, Kuzmina, Parenago, & Topchiev, 2004; Kheireddin, 2013; B. Li, Wang, Liu, & Xue, 2006; L Rapoport et al., 1997; Wang & Liu, 2013). Term Nanolubricant is said as a base oil or fully formulated lubricant have solid nanparticle suspended within (Martin & Ohmae, 2008; Saidur, Kazi, Hossain, Rahman, & Mohammed, 2011).

Since there are a lot of nanoparticles combination that can be altered and investigated, nanolubricant is said to have potential in solving problems that usually involve with sulphur and phosphorus content within traditional lubricant. Researchers also found that nanoparticles suspended in base oil could have multiple role that will improve the tribological performance of the base oil (Chou et al., 2010; Z. S. Hu et al., 2002; Nallasamy, Saravanakumar, Nagendran, Suriya, & Yashwant, 2014; Thakur, Srinivas, & Jain, 2016; Verma, Jiang, Abu Safe, Brown, & Malshe, 2008).

Apart from abundant of research on nanolubricant, it is still a challenge for researchers to achieve a perfect nanoparticle combinations as the tribological performance depends on multiple conditions including compatibility with base oil/lubricant, their sizes and morphologies, as well as their concentrations (Peña-Parás et al., 2015).

2.6 Nanoparticle effect in Lubrication

Inducing the nanoparticle provides a few effects to the lubrication especially between metal to metal contact. Among the effects that have been observed by researchers including ball bearing or rolling effect, protective layer effect, mending effect and polishing effect. These effects have been complied by Thirumalaikumaran (2017). Lee et al (2009), Wu et al (2007), Rapoport et al (2002) and Chinas-Castillo and Spikes (2003) have observed the rolling effect of nanoparticles in lubrication. Hu et al (2002), Xiaodong et al (2007), Ginzburg et al (2002), Zhou et al (1990) observed the protective layer effect from nanoparticles which the layer prevent friction and provide coating at the rough surfaces. Mending effect have been observed by Liu et al (2004) and Lee et al (2009) where the nanoparticles fill in the crack or asperities on the uneven surface. Lee et al (2009) and Tao et al (1996) have observed the polishing effect from the nanoparticles which the nanoparticles remove part of rough surface through abrasion and makes the surface smoother thus reduce the friction.

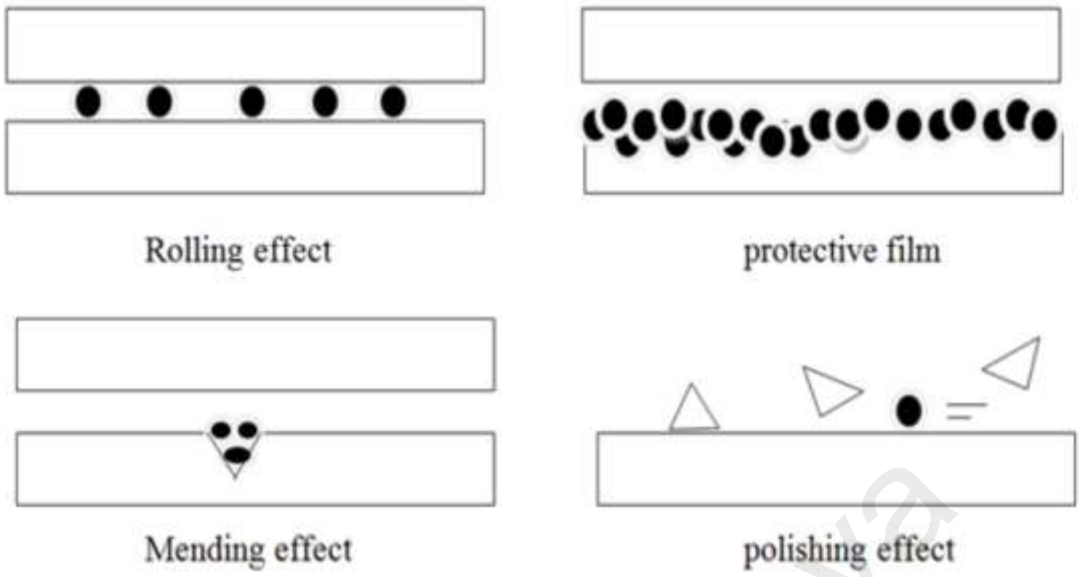

Figure 5: Role of nanoparticles in relative motion of two contacting surfaces (Thirumalaikumaran, 2017).

2.7 Nanoparticle Dispersion

Since nanoparticles are nano size thus very small, nanoparticles could remain dispersed in liquids by its Brownian motion. Brownian motion is a random motion of particles that was first observed by Robert Brown and later being proven by Albert Einstein (Einstein, 1905). However, upon time the particle could attract to each other and agglomerates into a larger particle group that could settle down into sedimentation due to gravity. This phenomenon also results in reduction of tribological performance which is loss of wear protection and friction reduction ability. For a high dispersion stability, particles will remain dispersed and not agglomerates at a longer period of time than nanoparticles with lower dispersion stability. In some cases, this poor dispersion stability could result in clogging (K. Lee, Y. Hwang, S. Cheong, L. Kwon, et al., 2009). Thus, this dispersion stability is one of the most important factors for an effective nanolubricants. For nanolubricant to compete with traditional lubricant in the mass market, this dispersion stability could be the important factor as the nanolubricant could be stored on the shelf for a long period of time thus detioriation of the tribological performance is not desired.

In this subsection, methods of nanoparticles dispersion and dispersion stability analysis will be discussed.

2.7.1 Methods of Nanoparticles Dispersion

Methods of nanoparticles dispersion could be crucial for a nanolubricant to have a stable dispersion stability. It is found that agitation of the IF-MoS2 enriched oil prior to testing would reduced the size of agglomerates (Rabaso, 2014). Some researchers have been using magnetic stirring (Rabaso, 2014), chemical agitation (Laad & Jatti, 2016), agitation using ultrasonic shaker (Thottackkad et al., 2012; Xie et al., 2015), agitation using mechanical ball milling agitation, ultrasonic probe (Alves et al., 2013; Battez et al., 2006; Battez et al., 2007; Mukesh et al., 2013; Viesca et al., 2011; H.-l. Yu et al., 2008; J. Zhou, Wu, Zhang, Liu, & Xue, 2000), and ultrasonic bath (Asrul, Zulkifli, Masjuki, & Kalam, 2013; K. H. Hu, Huang, Hu, Xu, & Zhou, 2011; Joly Pottuz et al., 2008).

2.7.2 Sedimentation Method for Dispersion Stability Analysis for Nanolubricants

For the analysis of the dispersion stability, different methods have been used by researchers includes sedimentation, spectral absorbency, zeta potential, and metallographic micrographs stability test. Sedimentation is said to be the simplest and less complex method among all. This method is also called “observation stability test” (Azman, Zulkifli, Masjuki, Gulzar, & Zahid, 2016). In this method, visual check on the sample is done and documented using photographs (Amiruddin, Abdollah, Idris, Abdullah, & Tamaldin, 2015; Koshy et al., 2015; Mukesh et al., 2013; Peng, Chen, et al., 2010; Peng, Kang, et al., 2010; Sui, Song, Zhang, & Yang, 2015, 2016). While this method is simple and less complex, it require a longer period of time to obtain the results. A result on dispersion analysis for a nanolubricant left in the shelf for a year could take the same one-year duration. Also, it is important that the temperatures, and surrounding conditions for all the considered samples are maintained throughout the period.

2.8 Four ball test

A lubricant might shows a different tribological performance when observed under different type of test conditions. This behaviour might be friction behaviour that could effected due to the relative orientation of the interacting surfaces (Falvo & Superfine, 2000). Popular type of triblogical test includes four-ball, ball-on-flat, pin-on-disk, cylinder-on-flat, piston ring on cylinder liner and block on ring (Figure below). Four ball test geometry using ASTM D2783 standard conditions are widely used especially in testing the EP characteristic and load carrying ability of a lubricant. (Abdullah et al., 2016; Chou et al., 2010; Viesca et al., 2011). Table 7 below which complied by Gulzar (2018) shows the summary of four-ball test and its conditions by different researchers.

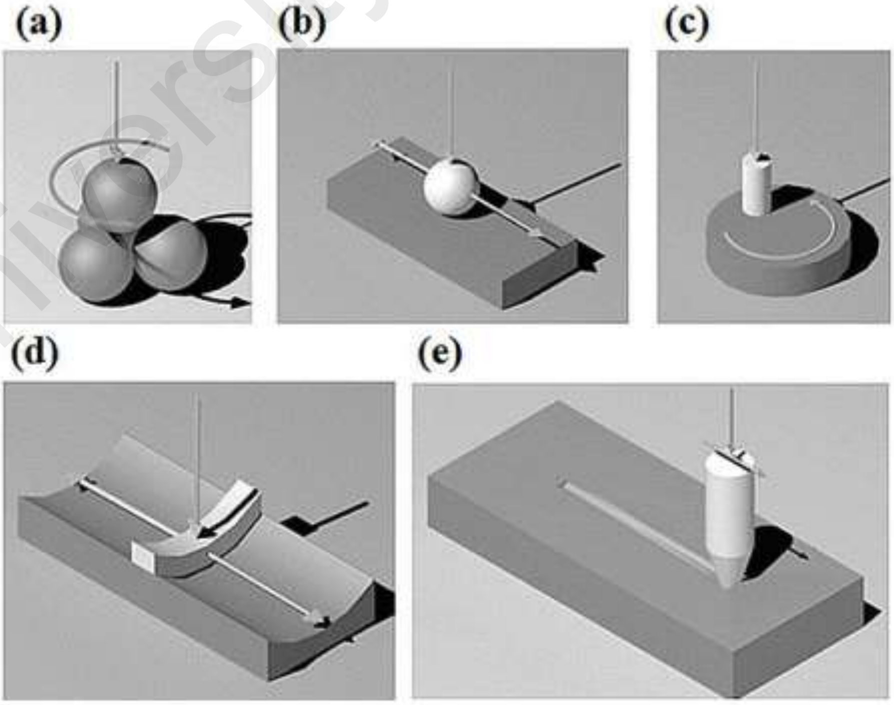

Figure 6:Commonly used tribo-testing geometric configurations (a) four-ball, (b) ball-on-flat, (c) pin-on-disk, (d) piston ring cylinder, (e) pin-on-flat (Gulzar, 2018)

Table 7: Compilation of four ball test condition by previous researches (Gulzar, 2018).

Nano particle	Oil	Test Duration (sec)	Temp (^{O}C)	Normal Load (N)	Speed (rpm)	Output Parameters	Reference
ZnO	PAO6	3600	75	392	1200	WSD	(Battez et al., 2006)
10/stage till weld	25	Varies/stage till weld	1470	ISL, LNSL WL, LWI,, WSD	(Battez et al., 2006)		
60SN base oil	1800	75	500	1000	Friction WSD,	(Ran et al., 2016)	
CuO	Liquid paraffin	900	60-70	392	1200	Friction WSD,	(Asrul et al., 2013)
PAO6	10 /stage till weld	25	Varies/stage till weld	1470	Friction, ISL, LNSL, WL, LWI, WSD	(Fernandez, Viesca, & Battez, 2008)	
Cu	Liquid paraffin	1800	-	300	1450	Friction WSD,	(Zhang et al., 2015)
PAO6	10 /stage till weld	25	Varies/stage till weld	1470	LWI, WSD ISL, WL,	(Viesca et al. 2011) ,	
MoS_2	SAE 20W-40	3600	75	392	600, 1200	WL, WSD	(Thakur et al., 2016)

10 /stage till weld	25	Varies/stage till weld	1470	LWI, WSD ISL, WL,	(Thakur et al., 2016)		
Al_2O_3/SiO_2	20# machine oil	1800	75	147	1,450	Friction, WSD	(Jiao et al., 2011)
CuO, ZnO, ZrO_2	PAO6	10 /stage till weld	25	Varies/stage till weld	1470	ISL, LNSL, WL, LWI, WSD	(Battez et al., 2008)
PTFE	150N group II base oil	3600	75	392	1200	WL, WSD	(Mukesh et al., 2013)
ZrO_2/SiO_2	20# machine oil	1800	75	147	1,450	Friction, WSD	(W. Li et al., 2011)
Ni	PAO6	10 /stage till weld	25	Varies/stage till weld	1470	ISL, LNSL, WL, LWI, WSD	(Chou et al., 2010)
hBN	SAE 15W40	10 /stage till weld	25	Varies/stage till weld	1760	WSD	(Abdullah et al., 2016)
MoS_2/TiO_2	Liquid paraffin	1800	25	300	1450	Friction WSD,	(K. H. Hu et al., 2011)
Fe, Cu, Co	SAE10	3600	25	150	1420	WSD, Friction	(Padgurskas, Rukuiza,

							Prosyčevas, & Kreivaitis, 2013)
TiO2	palm TMP ester	300	25	392,784, 1176, 1568	1200	WSD, Friction	(Zulkifli, Kalam, Masjuki, & Yunus, 2013)
$CaCO_3$	PAO+5 % palm TMP ester	3600	25	392	1200	WSD, Friction	(Zainal, Zulkifli, Yusoff, Masjuki, & Yunus, 2015)

CHAPTER 3 METHODOLOGY

3.1 Introduction

In this chapter, the setup of apparatus and the procedure involve in obtaining the desired data are explained in detail. A research methodology has been adopted to understand the tribological characteristics of the selected samples using a tribotester. Dispersion stability and wear scar diameter are also observed.

For an overview of the methodology, Figure below shows a flowchart as the reference to conduct the investigation.

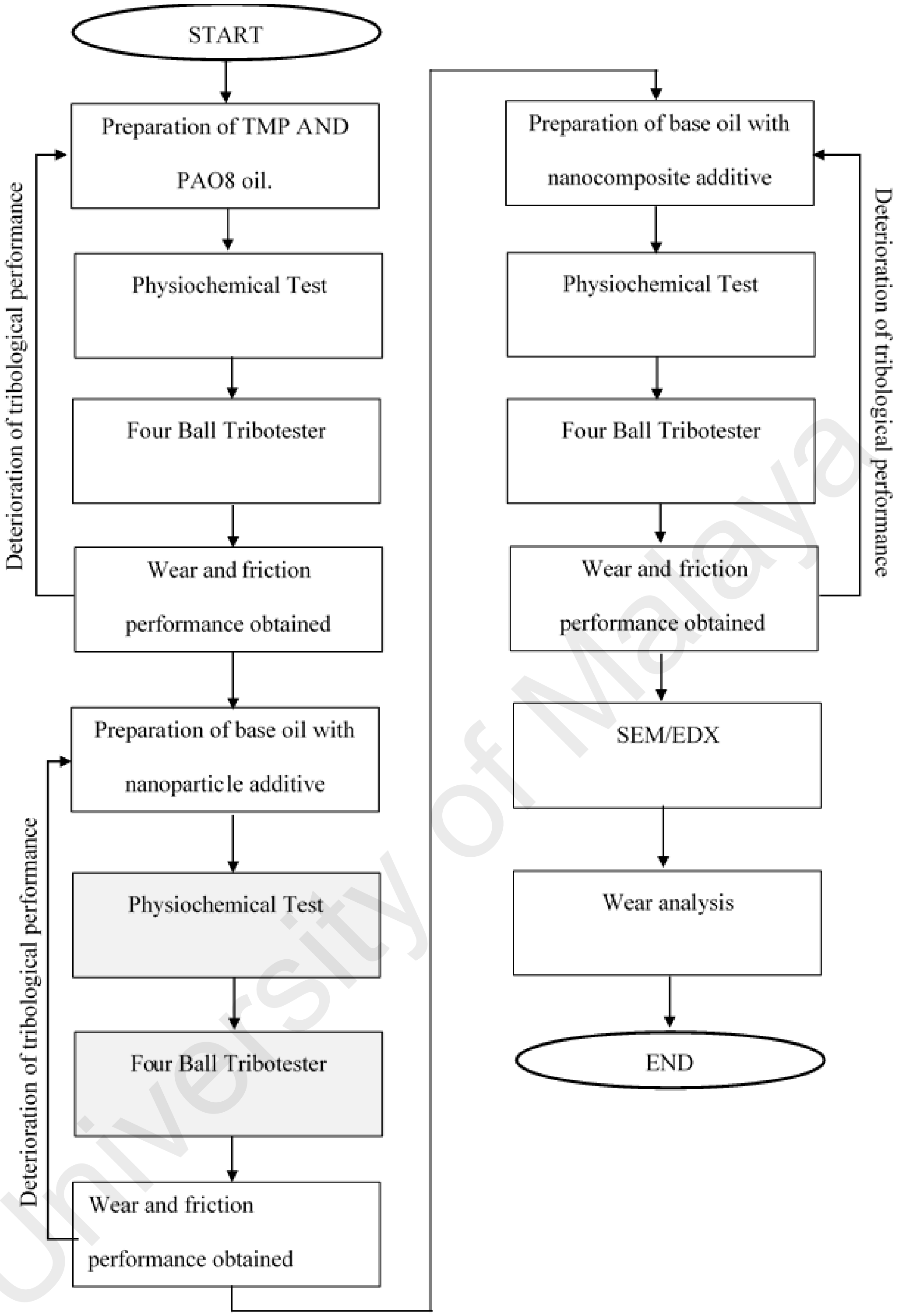

Figure 7: Flowchart for the methodology of this investigation.

3.2 Sample Preparation

The nanoparticles that will be investigated for this project is Titanium Dioxide (TiO_2) and Copper Oxide (CuO). Base bio oil selected for entire investigation is TMP ester. In this investigation, the TMP ester will be compared with conventional polyalphaolefin (PAO8) oil. For the nanoparticles additives of the base oil, the nanoparticles are mixed with the base oil using magnetic stirrer with speed of 700 revolution per minute for 60 minutes at room temperature. This project will include testing for pure base bio oil against conventional PAO8 oil, base bio oil with nanoparticle additive and base bio oil with nanocomposite additive.

3.3 Physicochemical Properties

Physicochemical properties that being investigated are density, viscosity and viscosity index. All samples were tested using Anton Paar Starbinger SVM 3000 Viscometer according to the ASTM D445 standard for viscosity and ASTM D4052 standard for density. This test apparatus has a reproducibility of 0.35% and a repeatability of 0.1%.

Viscosity index is obtained by measuring the viscosity change at different temperature. Kinematic viscosity at temperature of 40 C and 100 C were measured for all samples.

Figure 8: Starbinger SVM3000 Viscometer

3.4 Tribological Properties

In order to investigate the tribological behaviour of the samples for this project, four ball tribotester will be used.

3.4.1 Four Ball Tribotester

Figure 9: DUCOM Four Ball Tester TR-30H

A four ball tribotester uses configuration where three balls at the bottom and one ball at the top. The one ball at the top will spin according to the parameter set. For this project the four ball triboester used is DUCOM four ball tribotester ASTM4172. The ball material is alloy steel AISI5200.

Obtained data from the tribotester is used to investigate the tribological performance of each samples. The most important data captured during running the instrument is the coefficient of friction. After the completion of each test, the wear scars on the bottom of three balls were observed and measured using image acquisition system.

Table 8: Test Parameter

STANDARD	**LOAD (Kg)**	**DURATION (Sec)**	**TEMP. (^{O}C)**	**RPM**
ASTM D4172 B	40	3600	75±2	1200±60

Figure 10: AISI5200 Balls

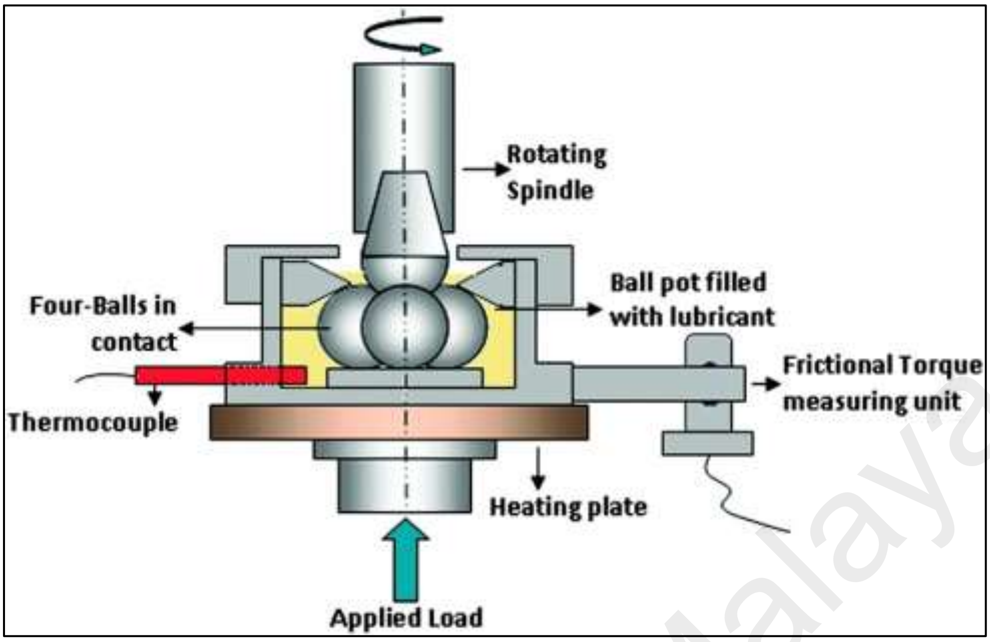

Figure 11: Four Ball Tribotester Arrangement

Figure 12: Image Acquisition System (Optical Microscope)

CHAPTER 4 RESULT AND DISCUSSION

4.1 Physicochemical Properties

Table 9: Measured physicochemical properties

Sample	Viscosity (mm^2/s)		Viscosity Index (VI)	Density, ρ (g/cm^3) $15^{O}C$
	$40^{O}C$	$100^{O}C$		
TMP	50.687	9.8674	+185.0	0.9201
TMP + 0.1 wt% CuO	51.449	10.004	+184.1	0.9211
TMP + 0.1 wt% TiO_2	51.579	10.025	+183.6	0.9211
CT11	52.068	10.079	+183.4	0.9213
CT12	51.509	9.9860	+184.6	0.9210
CT21	51.286	10.005	+183.2	0.9211

From table above, the addition of additives improves the viscosity of pure TMP at different temperatures. Lubricant with higher viscosity are more desirable to resist thinning. This is because at higher temperature lubricant become thinner and thicker at lower temperature. With proper introduction of additives, lubricant become thicker where it maintain better lubricating film between the moving surfaces. From the tested lubricant sample, the viscosity different between the samples are less than 1. This prove that the samples have same lubricating mechanism thus the frictional behaviour can be directly compared. From a research conducted by Binu et al, it shows that at particle weight percentage lower than 2% - 4%, the viscosity change is minimal and negligible (Binu, Shenoy, Rao, & Pai, 2014).

4.2 Tribological testing of base oil

TMP base oil and PAO8 were subjected to tribological test using four ball tribotester at temperature 75 °C with 1200 revolution per minute under 40kg load. Data obtain was recorded then analyzed.

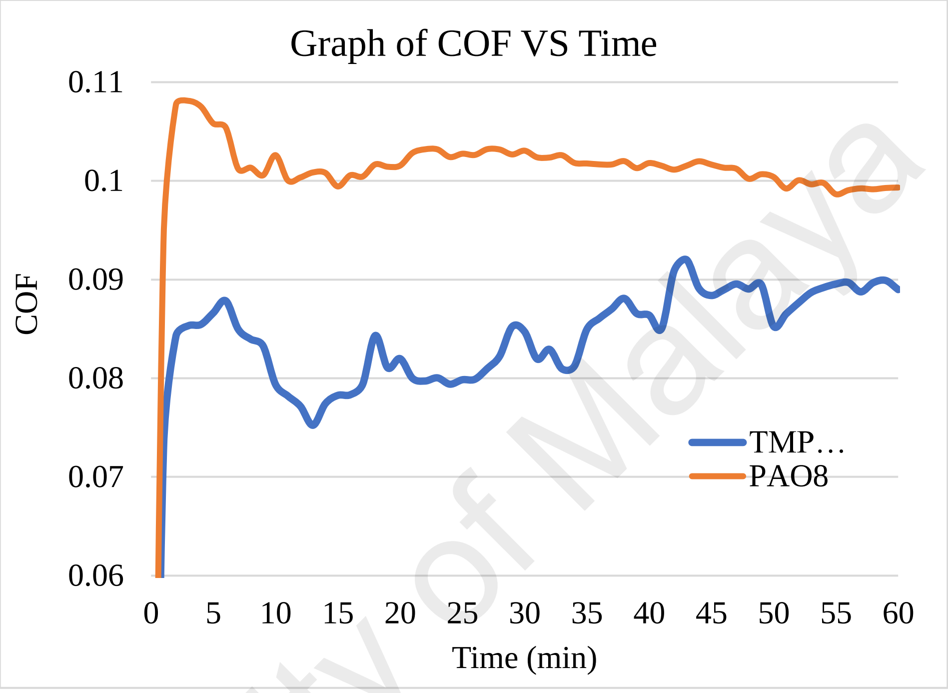

Figure 13: Graph of COF vs Time for PAO8 and TMP.

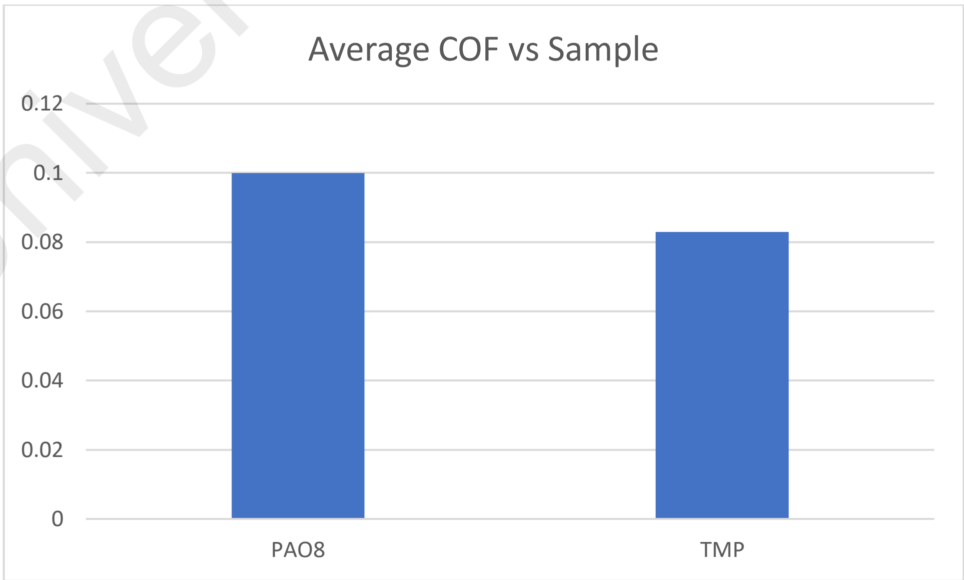

Figure 14: Comparison of average COF of PAO9 and TMP.

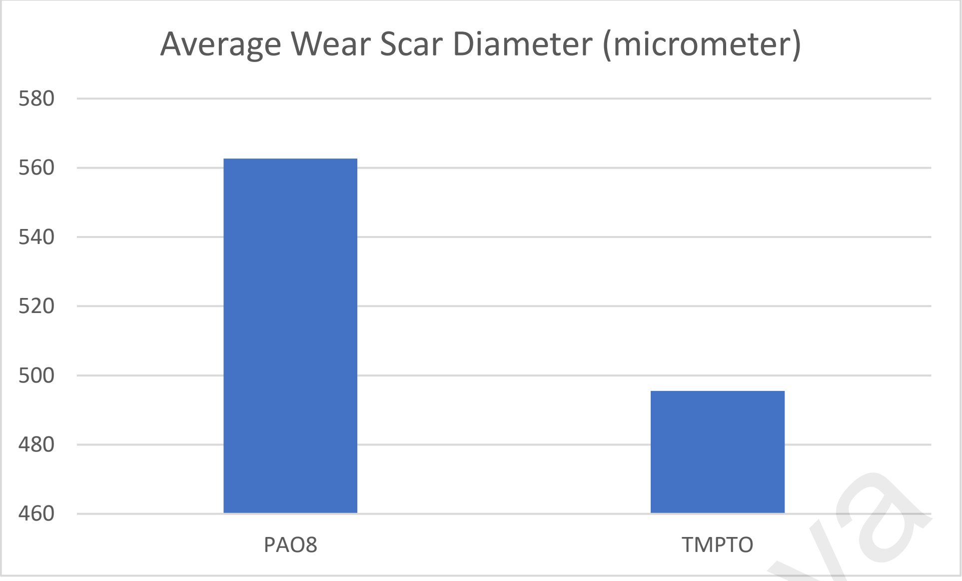

Figure 15: Comparison of Average WSD for PAO8 and TMP.

Figures above show the coefficient of friction (COF) and Wear Scar Diameter TMP base oil and polyalphaolefin PAO8 throughout the 60 minutes of the test. Result shows that TMP ester base oil have the advantage over the conventional PAO8 on both the Coefficient of Friction and wear scar diameter result. It is noted that the improvement of Coefficient of friction of TMP ester base oil is at around 20% compared to PAO8 and improvement of wear scar diameter is at around 12% compared to PAO8. Thus, TMP ester have shown a superiority in the subjected condition over the conventional PAO8. Further into the investigation, TMP will be used as base oil and baseline to investigate the effect of nanoparticle and nanocomposites to the coefficient of friction and wear scar diameter.

4.3 Tribological testing of Nanoparticle in TMP base oil

Nanoparticle of Copper Oxide (CuO) and Titanium Dioxide (TiO2) with concentration of 0.01 wt%, 0.1 wt% and 1.0 wt% in TMP base oil were subjected to tribological test using four ball tribotester at temperature 75 oC with 1200 revolution per minute under 40kg load. Data obtain was recorded then analysed.

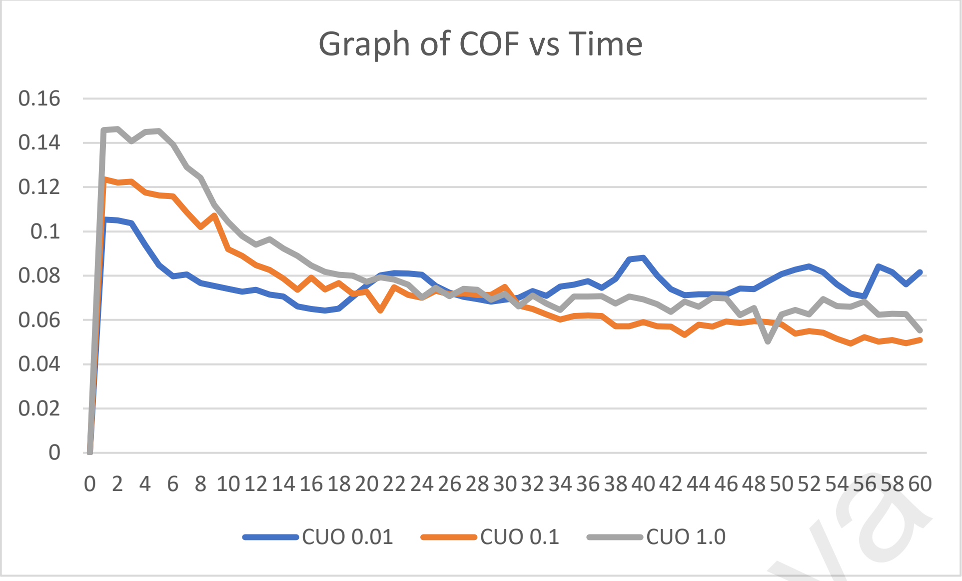

Figure 16: Graph of COF vs Time for TMP with CuO nanoparticle

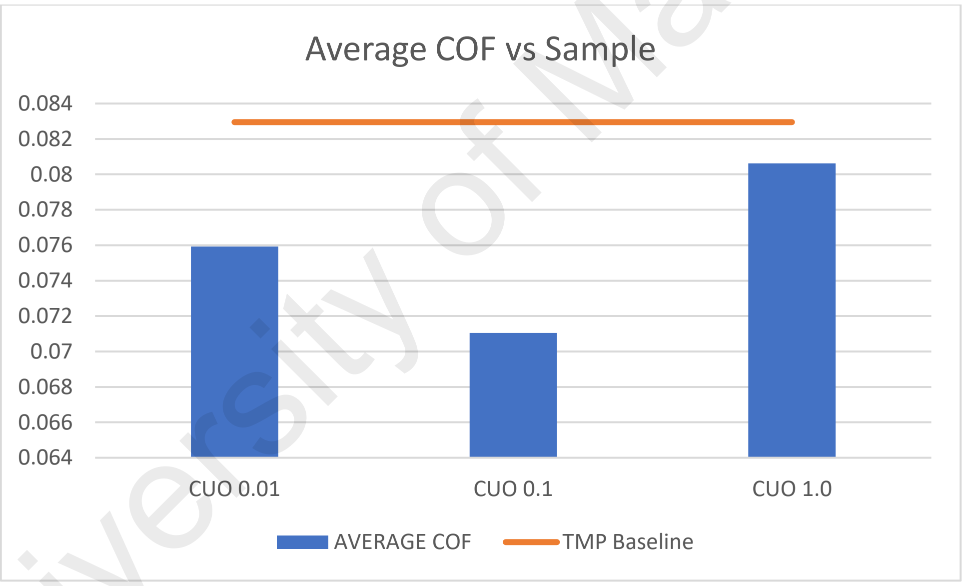

Figure 17: Average COF for TMP with CuO nanoparticle

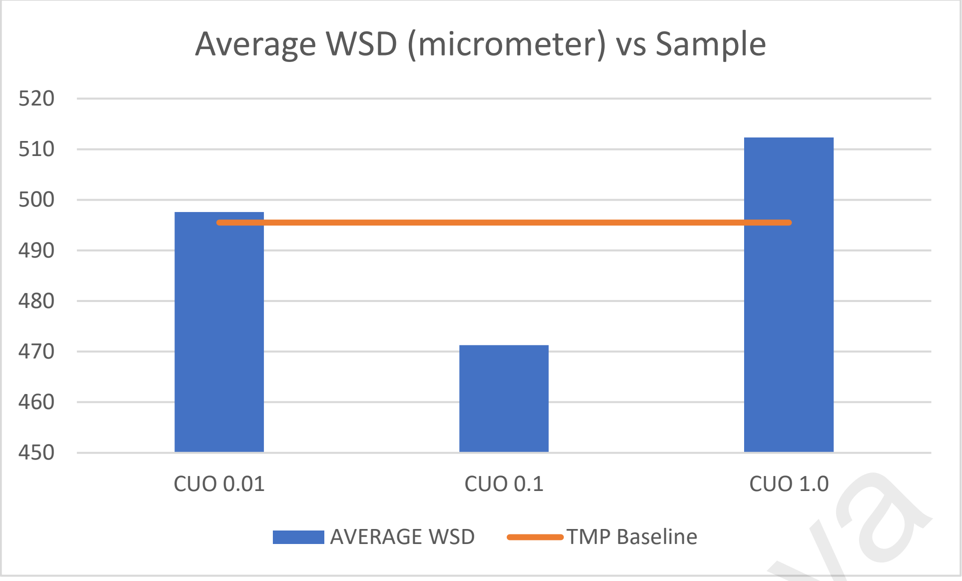

Figure 18: Average WSD for TMP with CuO nanoparticle

Figures above shows the coefficient of friction and wear scar diameter for Copper Oxide with different concentration. The sample of 0.01 wt% have average COF of 0.07592 which is around 6% improvement over the TMP baseline. Sample with 0.1 wt% have average COF of 0.07104 which indicates around 17% improvement over the TMP baseline and sample of 1.0 wt% have average COF of 0.08061 which is quite similar to the TMP baseline. For wear scar diameter sample of 0.01 wt% have average WSD of 497.6 µm which is around the same as the WSD of TMP baseline. Sample with 0.1 wt% have average WSD of 471.3 µm which is 5% improvement over the TMP baseline. The reduction in WSD by CuO nanoparticles may be attributed by the tribo-sintering of CuO nanoparticles on the wear surface. It then reduces the metal-to-metal contact that makes the surface smoother (Alves et al., 2016). Sample of 1.0 wt% have average WSD of 512.3 µm which shown a worse WSD against the TMP baseline. The sample of 1.0 wt% also shown a higher COF at the running in period compared to other samples. It is noted that the optimal concentration of 0.1 wt% of Copper Oxide have the lowest coefficient of friction and lowest wear scar diameter among all three sample.

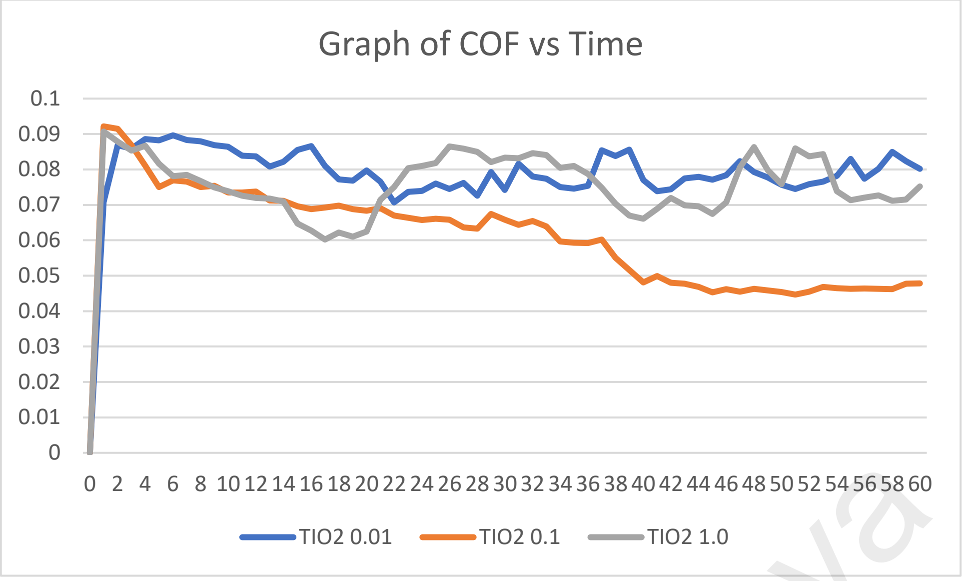

Figure 19: Graph of COF vs Time for TMP with TiO2 Nanoparticle

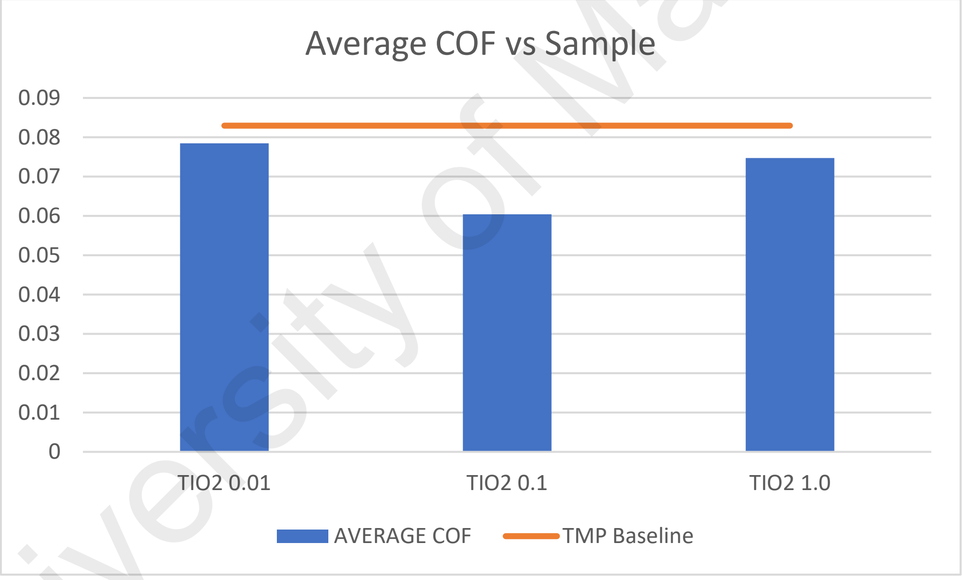

Figure 20:Average COF for TMP with TiO2 Nanoparticle

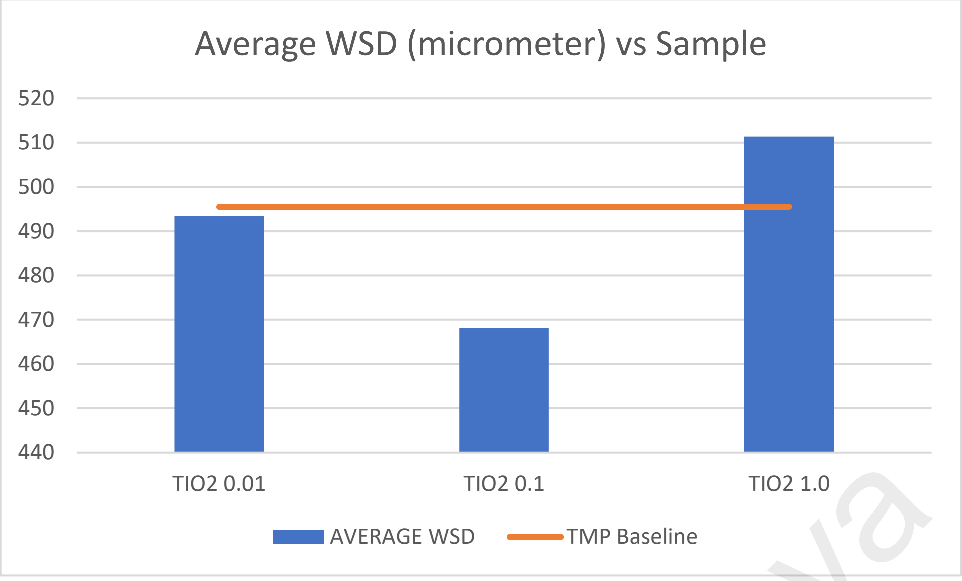

Figure 21:Average WSD for TMP with TiO2 Nanoparticle

Figures above shows the coefficient of friction and wear scar diameter for Titanium Dioxide with different concentration. The sample of 0.01 wt% have average COF of 0.07845 which is around 6% improvement over the TMP baseline. Sample with 0.1 wt% have average COF of 0.06563 which translate into around 26% improvement over the TMP baseline and sample of 1.0 wt% have average COF of 0.07475 which indicates improvement of around 11% over the TMP baseline. The findings are in line with findings by Gu et al (2009) by using the same Titanium Dioxide nanoparticle. For wear scar diameter sample of 0.01 wt% have average WSD of 493.4 μm which is around the same as the TMP baseline. Sample with 0.1 wt% have average WSD of 468.1 μm which indicates improvement of around 6% over the TMP baseline and sample of 1.0 wt% have average WSD of 511.4 μm which shown a worse WSD against the TMP baseline. From these results, It is noted that the concentration of 0.1 wt% of Titanium Dioxide have the lowest coefficient of friction and lowest wear scar diameter among all three sample. From previous study, it was concluded that the reduction in friction may be due to the fact that TiO_2 nanoparticles have low aspect ratio (Arumugam & Sriram, 2013).

For both Copper Oxide and Titanium Dioxide, the results indicates that the optimum concentration over the TMP base oil is at 0.1 wt%. This is in line with research conducted by Ting. et al (2014) conclude that the best friction-reducing effect of an additives is at concentration of 0.1 wt% and at higher concentration the friction coefficient increase gradually (Luo, Wei, Zhao, Cai, & Zheng, 2014). Thus, for the next part of the investigation, 0.1 wt% concentration of nanocomposites will be used to determine the optimum configuration ratio of the nanocomposites.

4.4 Tribological testing of nanocomposites in TMP base oil

Nanocomposite of Copper Oxide (CuO) and Titanium Dioxide (TiO2) with configuration ratio of 1 to 1 (CT11), 2 to 1 (CT21) and 1 to 2 (CT12) with 0.1 wt% in TMP base oil were subjected to tribological test using four ball tribotester at temperature 75 oC with 1200 revolution per minute under 40kg load. Data obtain was recorded then analysed.

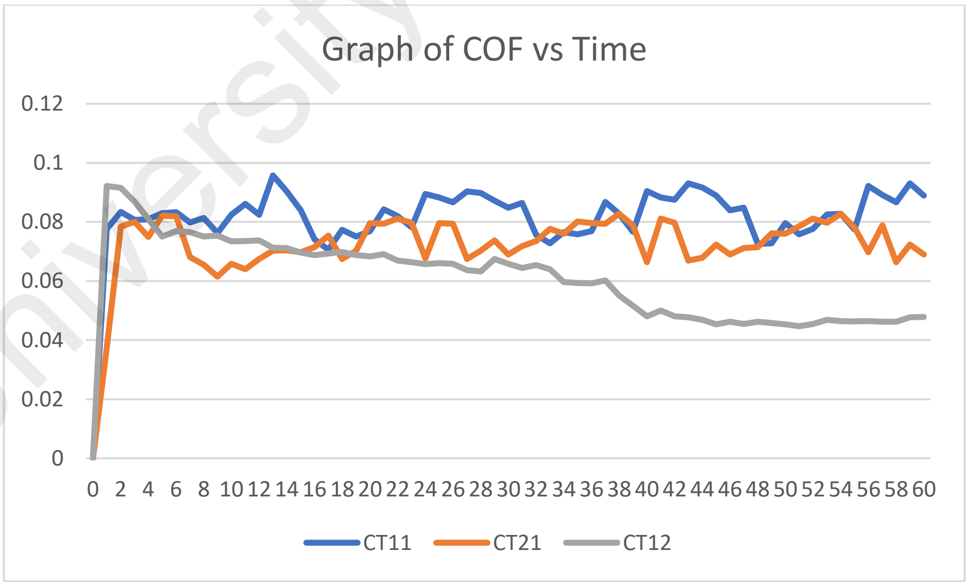

Figure 22: Graph of COF vs Time for TMP with CuO and TiO2 nanocomposite.

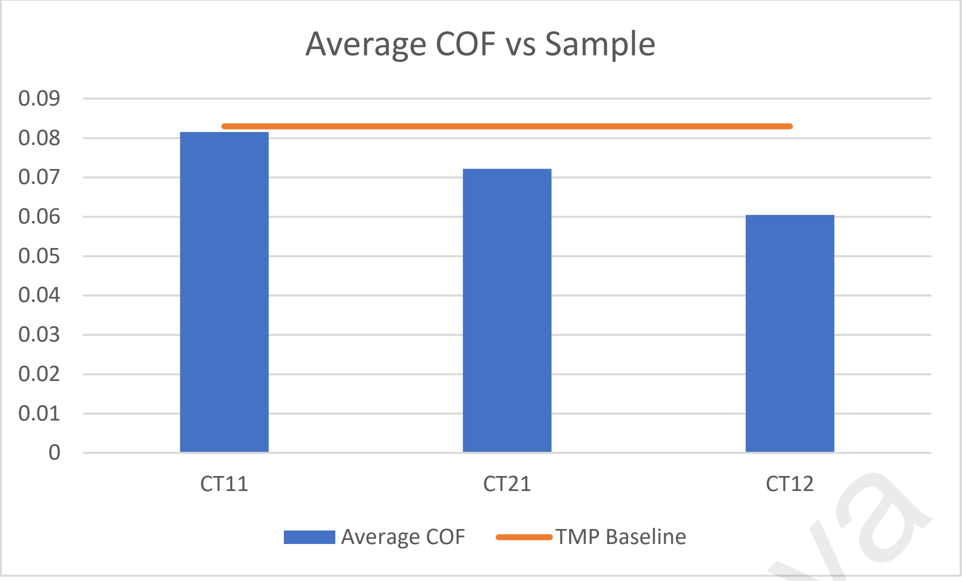

Figure 23: Average COF for TMP with CuO and TiO2 nanocomposite

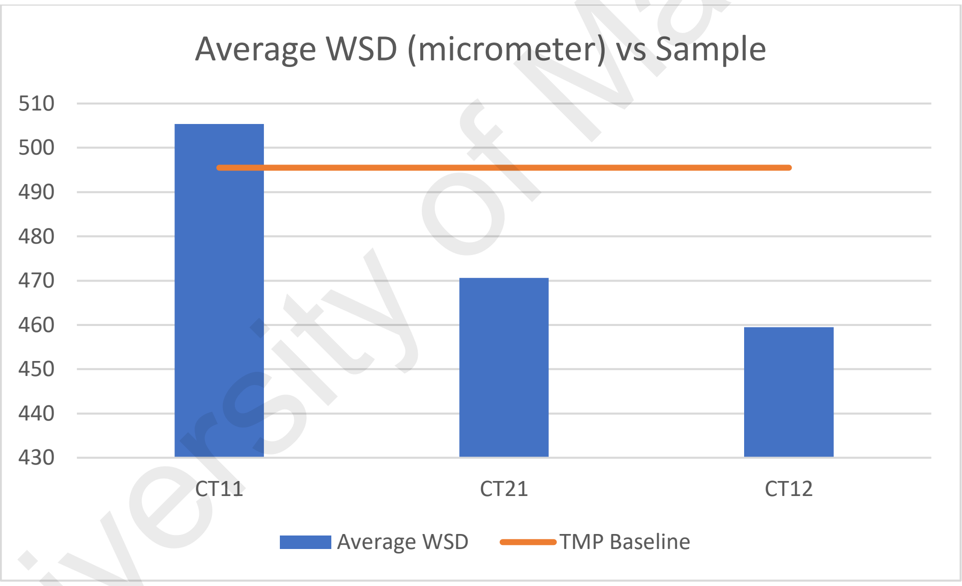

Figure 24: Average WSD for TMP with CuO and TiO2 nanocomposite

Figures above shows the coefficient of friction and wear scar diameter for nanocomposites of copper oxide and titanium dioxide with different configuration ratio. The sample with ratio of 1 to 1 have average COF of 0.08150 which is around the same as the baseline TMP. This could be because of the agglomeration of the nanoparticle which suggests that the combination ratio might not be optimal for tribological improvement. Sample with ratio of 2 to 1 of copper oxide to titanium dioxide (CT21) have average COF of 0.07218 which is around 15% improvement over the TMP baseline and sample with ratio of 1 to 2 of copper oxide to titanium dioxide (CT12) have average COF of 0.06043 which translate to around 37% improvement from TMP baseline. The improvement in the CT12 sample suggests that the nanocomposite have done its role as the friction modifier for the base oil.

For wear scar diameter sample with ratio of 1 to 1 have average WSD of 505.4 µm which is similar to the TMP baseline WSD. Sample with ratio of 2 to 1 of copper oxide to titanium dioxide have average WSD of 470.6 µm which is 5% improvement over the TMP baseline and sample with ratio of 1 to 2 of copper oxide to titanium dioxide have average WSD of 459.5 µm which is 8% improvement over the TMP baseline. The improvement in the CT12 sample suggests that the nanocomposite have done its role as the anti-wear for the base oil as well as reducing the metal-to-metal contact between the top ball and the bottom balls. It is noted that the sample of ratio of 1 to 2 of copper oxide to titanium dioxide (CT12) have the lowest coefficient of friction and lowest wear scar diameter among all three sample.

From the graph of COF vs time, it is found that the sample CT12 have a better stabilisation than the other sample thus making it a better nanocomposite in terms operating stabilisation up to 60 minutes. The stabilisation also indicates that the nanocomposite have done its role in rolling and acts as friction modifier. This rolling effect prevent metal contact. This is because of the spherical shape of CuO and TiO_2 (Gulzar, 2018). Arumugam and Sriram in 2013 had obtained the same result. They found a friction reduction of 15.2% when adding TiO_2 nanoparticles to chemically modified vegetable oil.

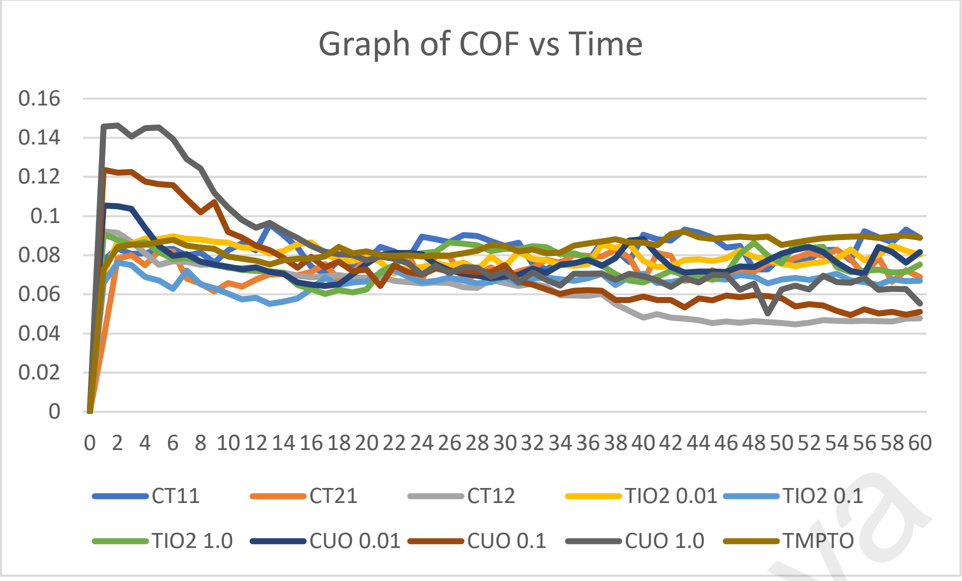

Figure 25: Graph of COF vs Time for all nanoparticle and nanocomposite samples

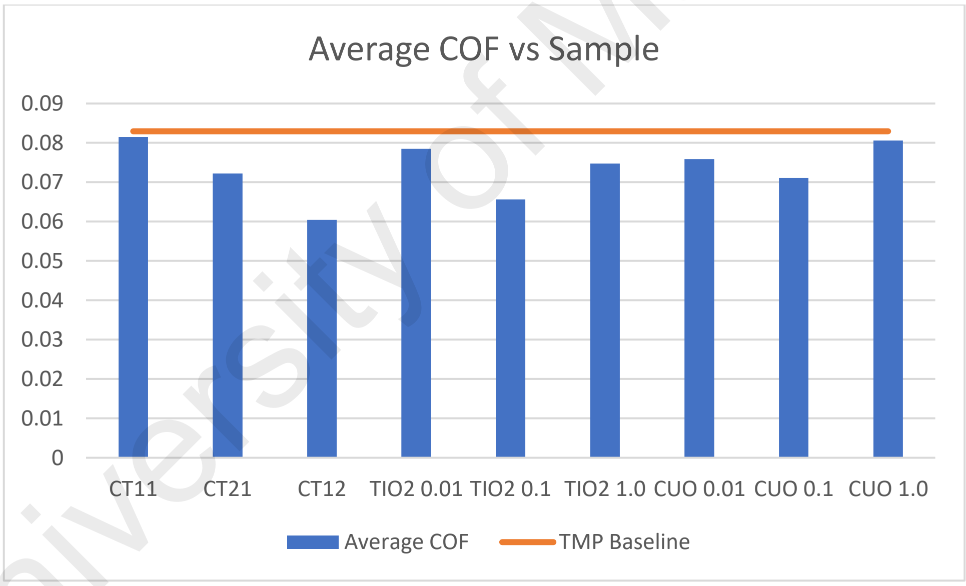

Figure 26: Average COF for all nanoparticle and nanocomposite samples.

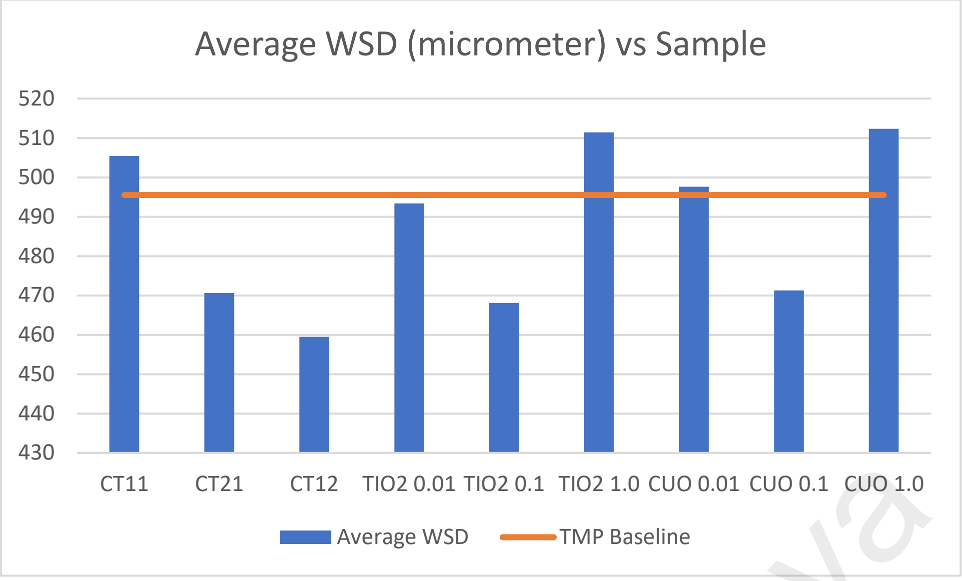

Figure 27: Average WSD for all nanoparticle and nanocomposite samples.

Figures above shows the coefficient of friction and wear scar diameter for all nanocomposite samples and nanoparticles samples of CuO and TiO_2. It is found that the sample of CT11 and CT21 have very similar COF with the COF of nanoparticles of CuO and TiO_2. This shown that the configuration ratio of 1 Copper Oxide to 1 Titanium Dioxide and 2 Copper Oxide to 1 Titanium Dioxide does not give much tribological improvement over the single individual type of nanoparticle. For sample CT12, the COF shown improvement over the COF of nanoparticles of CuO and TiO_2. This shown that the composite of both Copper Oxide and Titanium Dioxide at configuration ratio of 1 Copper Oxide to 2 Titanium Dioxide improves the tribological performance from the single individual type of nanoparticle.

For wear scar diameter, the sample of CT12 again shown the best result among all sample. Thus, further emphasise that the configuration ratio of 1 Copper Oxide to 2 Titanium Dioxide is the best among other configuration ratio. Sample of CT11 shown no improvement of WSD thus indicates further that the configuration ratio of 1 Copper Oxide to 1 Titanium Dioxide would not give any tribological improvement over the single individual type of nanoparticle. For sample CT21, the WSD shown some improvement over some individual nanoparticle samples, but the improvement of WSD is not as much as the sample CT12.

4.4.1 Scanning Electron Microscope and Energy Dispersive X-Ray Analysis

Further into the investigation, the balls for each CT11, CT21 and CT12 were subjected to Scanning Electron Microscope and Energy Dispersive X-Ray machine to analyse more on the wear and elements deposited on the balls. The results are as follows.

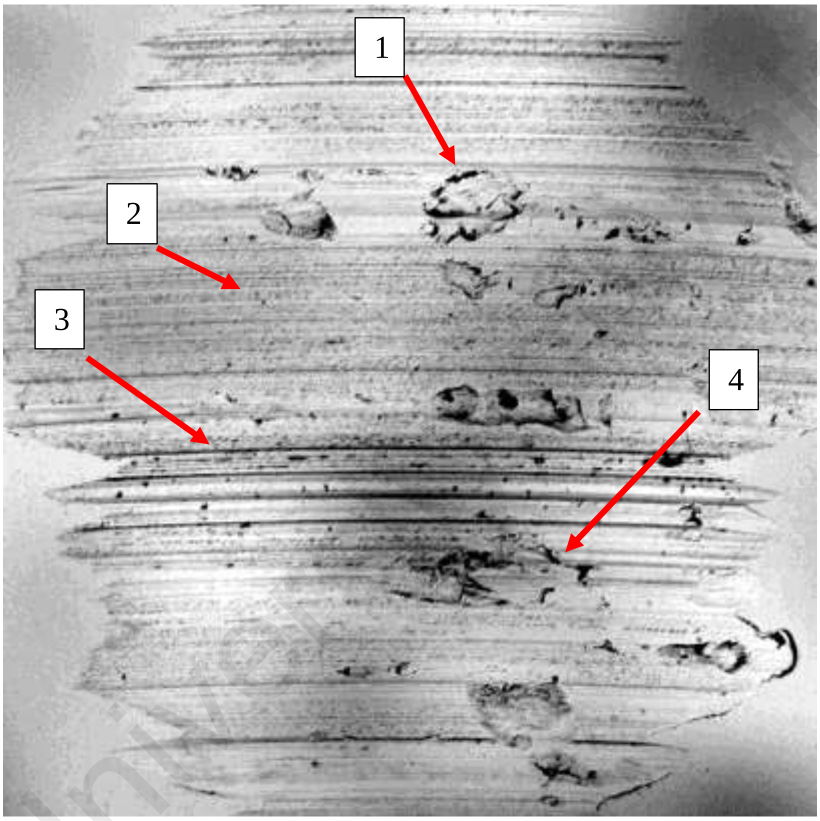

Figure 28: SEM photo for sample CT11.

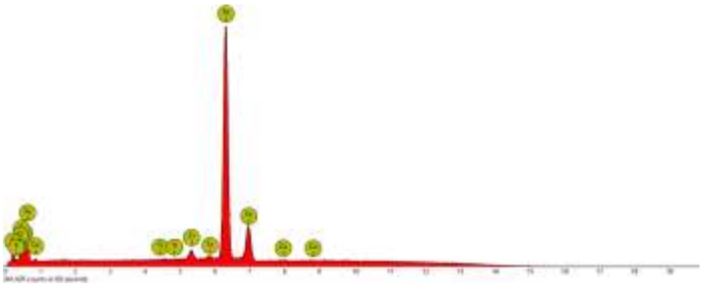

Figure 29: EDX analysis for sample CT11.

Table 10: Detail of elements from EDX of sample CT11

Element Number	**Element Symbol**	**Element Name**	**Atomic Conc.**	**Weight Conc.**
26	Fe	Iron	75.42	91.06
6	C	Carbon	15.16	3.94
8	O	Oxygen	7.28	2.52
24	Cr	Chromium	1.72	1.94
29	Cu	Copper	0.34	0.47
22	Ti	Titanium	0.08	0.09

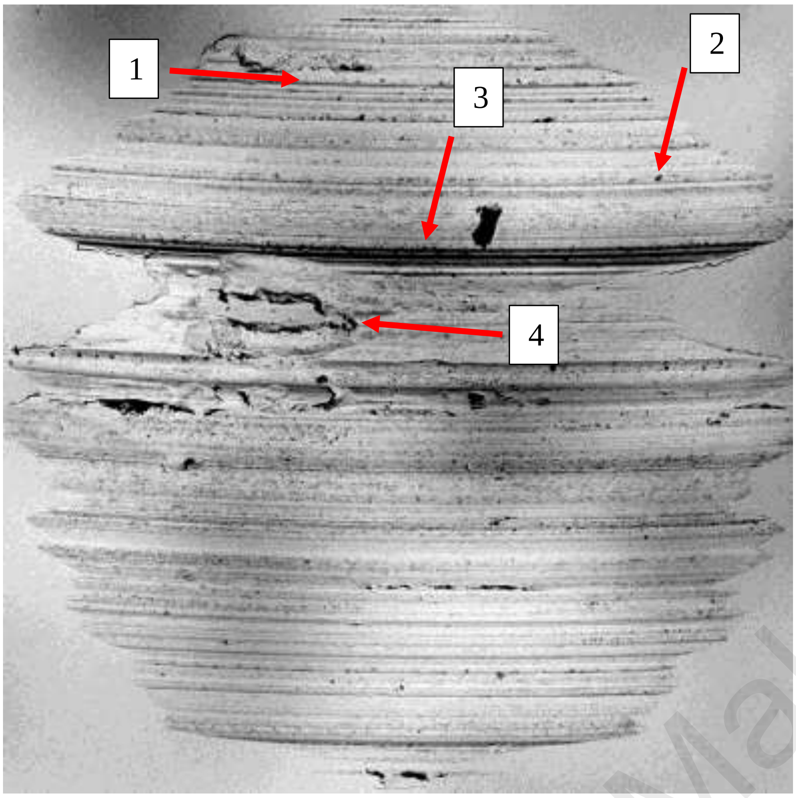

Figure 30: SEM photo for sample CT21

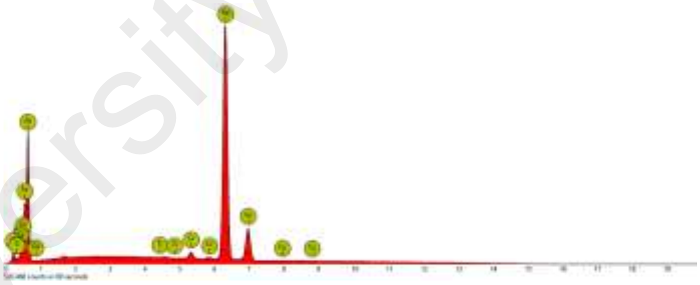

Figure 31: EDX analysis for sample CT21.

Table 11: Detail of elements from EDX of sample CT21.

Element Number	**Element Symbol**	**Element Name**	**Atomic Conc.**	**Weight Conc.**
26	Fe	Iron	76.40	92.06
6	C	Carbon	15.22	3.95
8	O	Oxygen	6.99	2.41
24	Cr	Chromium	1.18	1.33
29	Cu	Copper	0.15	0.20
22	Ti	Titanium	0.05	0.05

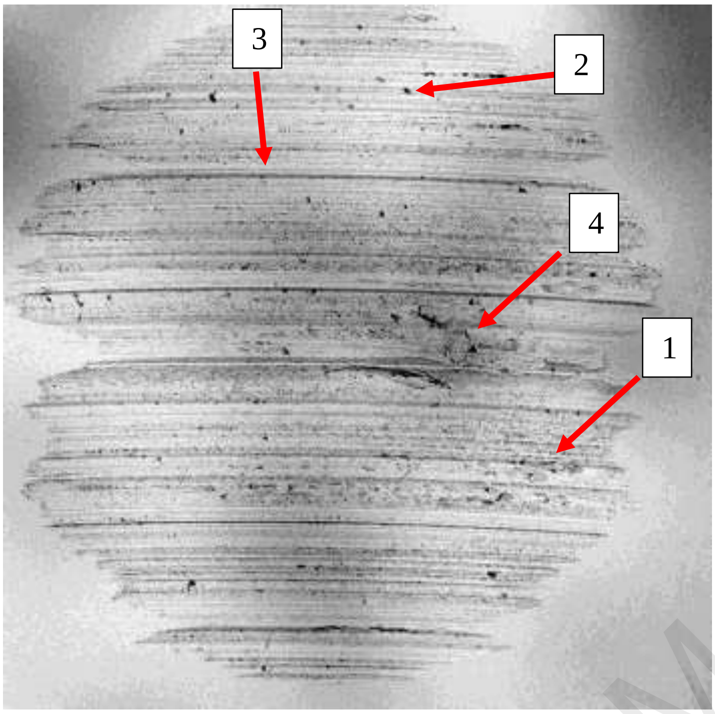

Figure 32: SEM photo for sample CT12

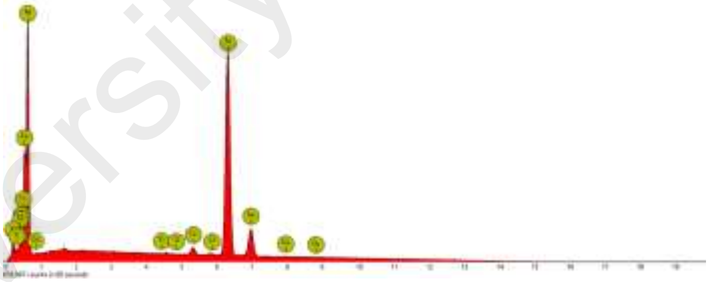

Figure 33: EDX analysis for sample CT12

Table 12: Detail of elements from EDX of sample CT12.

Element Number	**Element Symbol**	**Element Name**	**Atomic Conc.**	**Weight Conc.**
26	Fe	Iron	64.30	87.02
6	C	Carbon	22.14	6.44
8	O	Oxygen	12.14	4.71
24	Cr	Chromium	1.25	1.58
29	Cu	Copper	0.14	0.21
22	Ti	Titanium	0.03	0.03

Legend: (1) Delamination (2) Pitting (3) Abrasion (4) Adhesion

From the figure of SEM, it can be found that all sample indicates of pitting, delamination, abrasion and adhesion which are common type of wear found the metal-to-metal contact. However, the sample of CT12 shown a much smoother wear and less adhesion effect compared to sample CT11 and CT21. This further indicates the 1 to 2 of copper oxide to titanium dioxide is a better configuration ratio than 1 to 1 and 2 to 1.

From the EDX results, all samples shown a high iron (Fe) content which is the main composition of AISI5200 steel alloy ball. However, CT12 sample shown a lesser iron content among the samples which indicates a reduced metal-to-metal contact and adhesive behaviour. Another important aspect in the EDX results is the oxygen (O) content. The oxygen content in the sample CT12 is higher than the other samples. This higher oxygen content indicates that the nanocomposite have reduced friction effect by having a separation layer between the metals (J.A. Heredia-Cancino et al, 2008).

Both SEM and EDX results shown CT12 have a better tribological performance compared to other samples. This could be because of higher presence of Titanium Dioxide in the CT12 sample. This is in line with results obtained by Hernández Battez et al. (2008) where Titanium dioxide have shown around 15% improvement over the base oil while Copper Oxide only manage to improve around 3% over the base oil. Thus, a higher presence of Titanium Dioxide in a nanocomposite have a better the tribological performance.

CHAPTER 5 CONCLUSIONS

From the investigation conducted, tribological behaviour of TMP ester is tested against the conventional PAO8 using four-ball tribotester. The TMP ester produced an improvement in terms of tribology against the PAO8.

Addition of nanoparticles of Copper Oxide (CuO) or Titanium Dioxide (TiO2) improved the tribological performance of the TMP ester even more. It is also concludes that an optimum concentration of the nanoparticle are needed to ensure the nanoparticle played their role effectively. For this investigation, both CuO and TiO2 have optimum concentration of 0.1 wt%.

Combining the two Copper Oxide (CuO) nanoparticle and Titanium Dioxide (TiO2) nanoparticle into a nanocomposite which added into the TMP ester improved the tribological performance of the TMP ester. It concludes that in order for the nanocomposites to perform optimally, the right configuration ratio must be archived, For Copper oxide (CuO) and Titanium Dioxide (TiO2) nanocomposite, the configuration ratio of one Copper Oxide and two Titanium Dioxide produced the best tribological performance against other configuration ratio tested.

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APPENDIX

1. Schedule of work

	SEMESTER 2 SESSION 2018/2019													
Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Obtaining literature	■	■	■											
Article review		■	■	■	■	■	■							
Writing literature review				■	■	■	■	■	■					
Finalising Methodology										■	■			
Sample preparation												■	■	
Testing of sample														■

	SPECIAL SEMESTER SESSION 2018/2019													
Week	1	2	3	4	5	6	7							
Analysing test result	■													
Report writing		■	■	■										
Report amendment					■	■								
Report submission							■							