

**THERMAL ACTIVITIES IN NATURAL-OIL AND  
SYNTHETIC LUBRICANTS WITH TIO<sub>2</sub> ADDITIVES**

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**UNIVERSITI SAINS MALAYIA**

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# **THERMAL ACTIVITIES IN NATURAL-OIL AND SYNTHETIC LUBRICANTS WITH TIO<sub>2</sub> ADDITIVES**

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## DECLARATION

I, Noor Shafiatul Akmal binti Abdul Muein, thus declare that this thesis is my original work, completed after registering for the degree, and not previously included in a thesis or dissertation submitted to this or any other institution for a degree, diploma, or other qualification. I have studied the University's current research ethics rules and take responsibility for its implementation.



Signature: \_\_\_\_\_

Date: 24/07/2022

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## ABSTRAK

Keselamatan tenaga masa depan mungkin terancam oleh pergantungan dunia pada produk berasaskan petroleum dalam sektor pengangkutan dan perindustrian. Kadangkala, bahan-bahan ini dikembalikan ke alam sekitar, mengakibatkan pencemaran alam sekitar yang serius dan risiko. Pelincir berasaskan bio semakin terkenal sebagai pengganti berpotensi kepada pelincir berasaskan mineral kerana ia memainkan peranan penting dalam menyelesaikan masalah. Telah didedahkan bahawa pelincir berasaskan bio memberikan kualiti pelincir yang lebih tinggi berbanding dengan pelincir mineral konvensional, dengan kebolehbaharuan dan kebolehbiodegradan merupakan ciri-ciri mereka yang paling berfaedah. Terdapat keperluan penting untuk mengkaji semula literasi sedia ada untuk menyelidik potensi aplikasi pelincir berasaskan bio. Tujuan kajian ini adalah untuk menekankan potensi pelincir bio untuk pelbagai jenis aplikasi berdasarkan penyelidikan yang dijalankan sepanjang dekad sebelumnya dan diterbitkan dalam jurnal. Kajian ini juga menyerlahkan banyak aplikasi di mana potensi penggunaan pelincir berasaskan bio telah dikaji. Berdasarkan penemuan asas, adalah mungkin untuk membuat kesimpulan bahawa pelincir berasaskan bio adalah alternatif yang boleh dilaksanakan kepada pelincir berasaskan petroleum untuk beberapa aplikasi kerana ketersediaan sifat yang luas yang diperlukan untuk aplikasi tertentu. Bagi sesetengah aplikasi, bagaimanapun, pengubahsuaian kimia adalah perlu untuk mengatasi batasan seperti ciri suhu rendah yang lemah dan kestabilan oksidatif. Dengan minyak asas dan komposisi pakej tambahan yang sesuai, pelincir berasaskan bio boleh mengatasi pelincir konvensional.

## **ABSTRACT**

The transportation and industrial sectors' reliance on petroleum-based products may pose a threat to future energy security. On occasion, these compounds were returned to the environment, resulting in severe contamination and threats to the environment. Bio-based lubricants are gaining popularity as viable substitutes for mineral-based lubricants since they play an essential role in resolving the issues. It has been discovered that bio-based lubricants are superior to conventional mineral lubricants in terms of lubricating properties, with renewability and biodegradability being their most favourable traits. It is crucial to evaluate the available literature in order to investigate the prospective uses of bio-based lubricants. The objective of this study is to highlight the potential of bio lubricants for a wide range of applications based on research published in peer-reviewed publications over the past decade. This study also highlighted the several applications for which the potential use of bio-based lubricants has been investigated. On the basis of the basic findings, it is possible to infer that bio-based lubricants are a viable alternative to petroleum-based lubricants for a variety of applications due to their extensive availability of qualities required for specific applications. To overcome constraints such as poor low-temperature properties and oxidative stability, chemical modification is required for some applications. With the right composition of base oil and additives, bio-based lubricants can outperform traditional lubricants

## CHAPTER 1

### INTRODUCTION

#### 1.1 Introduction

In the production of various biopolymers and resins, conjugated fatty acids/vegetable oils are utilized as efficient monomers. They are notably important in the paint and food industries, but also play a role in the development of high viscosity lubricants for the lubricant industry. To improve their qualities, vegetable oils have been heated (Tulashie & Kotoka, 2020). The two different kinds of fatty acids that can be found in vegetable oils are saturated and unsaturated fatty acids. Palm oil is a versatile oil that may be used for both culinary and non-edible applications. It is commonly used as a cooking oil in processed foods like chocolate bars, ice cream, and cookies, among other things. When compared to olive or sunflower oil, palm oil has around 40–50 percent more saturated fatty acids. In spite of this, there has been much debate concerning the consequences that palm oil has on human health. Vegetable oils are frequently utilized as lubricants in industrial applications such rolling, cutting, drawing, and quenching due to their great lubricity, good anticorrosion qualities, superior viscosity–temperature relationships, and low evaporation losses. Specifically, metals are used in rolling, cutting, and drawing processes (Sneha et al., 2019).

Automotive and industrial lubricants are the two most common lubricant applications. The market for soybean oil lubricants will be driven by environmental concerns, while it will be constrained by economic and performance factors. Mineral oils will be less expensive and will meet OEM performance criteria. The addition of TiO<sub>2</sub> nanoparticles to engine oil greatly decreases friction and wear, hence enhancing the engine oil's lubricating characteristics. UV spectrometer dispersion investigation of TiO<sub>2</sub> nanoparticles in lubricating oil reveals that TiO<sub>2</sub>

nanoparticles possess good stability and solubility in the lubricant and enhance the lubricating qualities of engine oil (Cortes et al., 2020).

One of the main flaws of bio lubricants is low oxidative stability. When one of these lubricants is applied between two contacting metal surfaces, a stable lubricating layer should form. When the bio lubricant is oxidized, the lubricating coating becomes unstable. Esterification, epoxidation, and transesterification, as well as hydrogenation and mixtures of various chemicals, have been employed to address these oxidative stability issues. The addition of antioxidants to oils is one of the most efficient methods for enhancing their oxidative stability. Antioxidants are utilized to prevent or reduce oil oxidation, hence prolonging its shelf life. Vegetable oil-derived lubricants are superior due to enhanced properties such as high viscosity, flash point, and pour point. Vegetable oils nevertheless have limits that need the use of other solvents (Durango-Giraldo et al., 2022).

Depending on the origin of the raw materials used to produce them, vegetable oils can be derived from edible or inedible oils. Environmentally, bio lubricants generated from non-food oils are preferable because they may be produced utilizing waste crops. Although several raw material sources are being researched at present, the market for bio lubricants is particularly specialized. Esterification/transesterification, epoxidation, and hydrogenation are among the chemical processes used to transform feedstocks into bio-oils. This literature review explains these stages (Durango-Giraldo et al., 2022).

Despite the advantages, bio-based lubricants are not yet widely used because of serious problems with their performance, production scale, and absence assistance. When it comes to oxidation chemical stability properties, several bio lubricants fall short, especially crude

vegetable oils. However, these deficiencies can be corrected by making the necessary alterations and additions to the chemical composition. Protocols for the development and deployment of plant biotechnology in ways that are economically viable, socially valuable, and ecologically sustainable will arise from process and interpret between the manufacturer, environmental organizations, and government authorities. In the long run, these kinds of activities can lead to adaptive assessment and control of the environment, which has in turn can help push biotechnologies forward (Syahir et al., 2017).

The main objective of this study is to provide enough information regarding the thermal activities in natural-oil and synthetic lubricants with TiO<sub>2</sub> additives. Tribological aspects, such as lubricant characteristics, friction, and wear, are also treated. Formulation of lubricants requires fundamental knowledge of these factors. This is essential, as not all lubricants can be treated equally. Most published review papers focused on the study of new feedstocks and modification strategies for vegetable oils. Regarding the potential of bio-based lubricants for various applications, an evaluation is required. This is essential, as not all lubricants can be treated equally (Arumugam et al., 2014).

The effectiveness of bio lubricant films can be evaluated indirectly by tribological testing. This article provides a literature overview of palm oil for use in bio lubricants, focusing on the transesterification process and its associated processing parameters (such as molar ratio, stirring, temperature, and pressure). Furthermore, the impact of additives and the palm oil's physicochemical properties are examined (Yunusov et al., 2019).

## 1.2 Problem statement

Plant-oil has been known for its non-toxic and bio-compatible used for lubricants in recent years mainly due to its sustainable, renewable, and biodegradable for large range industrial applications such as plasticizers, stabilizers, and anti-oxidative agents. 80 to 90 percent of lubricating oils are made up of petroleum hydrocarbon distillate, while the remaining ten to twenty percent is made up of additives. Oil's carbon content can be lowered, and friction raised by adding TiO<sub>2</sub>. Therefore, the main objective of the present paper is to know either plant-oil comparable or not with the bio synthetic, to enhance the thermal expansion properties of selected additives plant-oil and aiming for the better understanding of the epoxidizing reactions on selected filled-additives plant-oil.

## 1.3 Objectives

- i. To study the oxidizing reactions on TiO<sub>2</sub> additives with plant-oil.
- ii. To determine the thermal expansion properties of TiO<sub>2</sub> additives with plant-oil.
- iii. To compare the TiO<sub>2</sub> additives plant-oil with the synthetic lubricants.

## 1.4 Scope of Work

- i. Vegetable oils that used in the experiment are red palm oil, coconut oil, sunflower oil, and soybean oil.
- ii. Motor engine oil was used as a synthetic lubricant.
- iii. Viscosity tests, pycnometer test and DSC analysis were used to conduct the tribological tests.

## **Chapter 2**

### **LITERATURE REVIEW**

#### **2.1 Lubricating oil**

The purpose of the lubricant is to reduce the deterioration of the components caused by their interaction. Traditional lubricating oils have a problem with degradation. Decomposition harms the ecology because it is poisonous and pollutes the atmosphere. Since they are not prevalent in the food supply chain, non-edible fuels are viable solutions for this problem. Due to its applicability for lubrication reasons, synthetic oil is one of the most widely used oil-based products. As a result of seepage, synthetic oils pose a risk of contaminating aquatic environments after use. This poses a few sustainability concerns. Therefore, it is necessary to find an alternative solution that can replace mineral oil. Considering these factors, the author concentrated on the search for an alternative to conventional oil. Bio lubricant is the resources that can be one of the key roles in boosting sustainability, as its use becomes more economical and natural. Bio lubricant is more biocompatible than synthetic lubricant or mineral oil, however it lacks the same advanced qualities as traditional lubricants (Singh et al., 2021).

#### **2.2 Vegetable oils**

Chemicals formed from vegetable oils like soybean, red palm oil and sunflower can be utilized in the production of countless industrially significant biomaterials, including plasticizers, biofuels, bio lubricants, packaging materials, adhesives, printing inks, paints, and coatings. Depending on industrial needs, vegetable oils can be easily converted into functional materials through one-step/multi-step techniques including a variety of chemical processes (Sánchez et al., 2011). This is because vegetable oils are predominantly composed of a triglyceride ester of long-chain fatty acids (mainly unsaturated). A reaction at the carboxy

group of fatty esters is one of the principal routes of chemical transformation for vegetable oils. Hydrolysis and transesterification occur at the carboxy group of fatty esters during the reaction. Vegetable oils undergo transesterification, a reaction with short-chain alcohols like methanol or ethanol, to generate methyl or ethyl esters of fatty acids (used as biofuel) and glycerol. The development of bio lubricants from trans esterified vegetable oils has been the topic of much attention in recent years. Hydrolysis of vegetable oils or trans esterified vegetable oils yields fatty acids, which can be used as a starting material in the synthesis of fatty amines, amides, and alcohols. Glycerol, which is created through transesterification or the thorough hydrolysis of vegetable oils, has many industrial applications. Glycerol is utilized in numerous industries, including the culinary, pharmaceutical, cosmetic, liquid detergent, antifreeze, and toothpaste sectors (Karmakar et al., 2020).

In place of mineral oil, vegetable oils can be used as lubricants since they are environmentally, biodegradable, and made from renewable raw materials. Thus, the primary disadvantage of using vegetable oils is that they have a low oxidation stability. According to the findings of certain researchers, additives in lubricating oil play a crucial function in decreasing friction and wear on surfaces that touching each other (Rajaganapathy et al., 2020).

Vegetable oils are one of the most popular alternatives to conventional cutting fluids due to their accessibility, affordability, and biodegradability. Vegetable oils that are user-friendly also have additional benefits, such as biodegradability, accessibility, and cost. Researchers are investigating the use of coconut oil, sunflower oil, canola oil, sesame oil, etc. in applications such as machining. Considering these features, exclusive research is being conducted on vegetable oils as an eco-friendly alternative to conventional lubricating fluid for a variety of applications (Sofiah et al., 2021).



### 2.2.1 Sunflower oil

The seeds of the sunflower are used to extract the oil that is used in cooking (*Helianthus Annuus*). Most of the oil comes in the form of a triglyceride, which is made up of four different types of acids: palmitic acid (which is saturated), stearic acid (which is also saturated), oleic acid (which is monounsaturated), and linoleic acid (polyunsaturated). It has been discovered that among these fatty acids, the high oleic acid, which has a concentration of 82 percent oleic acid, is appropriate for use as a lubricant because it possesses properties such as high oxidation stability and lubricity. Because it contains a high proportion of unsaturated fatty acids, sunflower oil has a high viscosity even when it is cold (Negi et al., 2021).

In sunflower oil, the addition of TiO<sub>2</sub> nanoparticles reduced the viscosity, in contrast to the effect of SiO<sub>2</sub> nanoparticles. Both 0.25 % and 0.50 % TiO<sub>2</sub> concentrations exhibited the same pattern of behaviour in terms of the viscosity. At a concentration of 1% TiO<sub>2</sub>, the fluid exhibited the behaviour with the least amount of viscosity. A similar pattern of activity was seen when the concentration of TiO<sub>2</sub> nanoparticles was varied from 0.75 % to 1.25 %. Shear thickening behaviour was observed when TiO<sub>2</sub> was added, even though the viscosity fell because of the addition of TiO<sub>2</sub>. This was because the power-law index was greater than 1. It is common knowledge that the size of the nanoparticles and their concentration can influence the rheological properties of colloidal suspensions like oil/nanoparticle systems (Cortes et al., 2020).

### **2.2.2 Palm oil**

The high concentration of saturated fat (Palmitic acid) in palm oil, along with the presence of monounsaturated oleic acid as a major component, makes it an excellent choice for use in the production of lubricant. For instance, it's not very stable when heated or exposed to oxygen. Palm oil comes from plantations of the *Elaeis guineensis* palm tree (*Elaeis guineensis*). The genus *Elais* in the palm family *Arecaceae* contains two noteworthy palm species. Palm oil is a fantastic substitute for mineral oil, which is used in many industrial processes. Researchers have conducted numerous experiments and investigations to determine palm oil's potential technical applications. When compared to other main vegetable oils like soybean and rapeseed, palm oil has the lowest production cost per tons. In comparison to other bio-based lubricants, palm oil is superior since its crops are more environmentally friendly. Fruit can be harvested from a cultivated palm tree starting in its fourth year and continuing for another 40-50 years. The biodegradability, excellent lubricating characteristics, high viscosity indices, low volatility, and high flash points of palm oil have all been lauded by other authors (Durango-Giraldo et al., 2022).

### **2.2.3 Soybean oil**

Soybean oil has been used as a bio lubricant in a number of different types of manufacturing. The machining industry could drastically cut its energy usage if biomimetics were included into the process. It is expected that the use of properly planned and prepared bio-lubricants derived from soybean oil will reduce energy consumption in an environmentally positive way. Using both practical and theoretical methods, this work examines the potential of bio-lubricants derived from soybean oil to reduce specific cutting energy in biomimetic intermittent turning. Epoxidized soybean oil (ESBO) and soybean oil were found to be the bio

lubricant's base oil (SBO). Both the *Procambarus clarkia* and the *Odontodactylus scyllarus* were examined to further biomimetic machining. This investigation revealed how the volume ratio of ESBO to SBO affected the base oil's viscosity and thermal stability. Using the proposed prediction methods, this work anticipated and evaluated variations in viscosity and the amount of base oil that remained after biomimetic machining. For the purpose of evaluating the efficiency of the bio lubricant made from soybean oil, a theoretical model was constructed. Specific cutting energy can be lowered by selecting optimal combinations of the volume ratio of ESBO/SBO and the element area of the bio-inspired microstructure on the tool's surface. The performance of bio-lubricants depends on maintaining a relatively high average level of base oil (Cui et al., 2021).

#### **2.2.4 Coconut oil**

Because of their high level of oxidation resistance and biodegradability, vegetable oils like coconut oil have been the subject of a significant amount of investigation in recent years. This has led to the development of new lubricant uses for these oils. Due to the high oxidative stability of coconut oil, it can still be utilized to a great extent as a base fluid. Because oxidative degeneration begins at a lower temperature than thermal degradation, this particular physical feature is vital for the use of vegetable oils as industrial lubricants. Coconut oil can nevertheless be utilized to a significant degree as a base fluid, particularly in areas that have a warm temperature (Sajeeb & Rajendrakumar, 2019). Because coconut oil has a low initiation temperature for thermal disintegration at 257 degrees Celsius and a high pour point of 23 degrees Celsius, it is not a good option for use in places that suffer colder climates. In addition, it is advantageous to use coconut oil as a base fluid for the dispersion of additives since coconut oil is a good base fluid (Sofiah et al., 2021).

### 2.3 Reformulation with additives

The manufacturing of lubricants entails blending a base oil with additives that either enhance the oil's inherent capabilities or impart new performance features. Vegetable oils have several disadvantages, the most significant of which are their poor thermo-oxidative stability and poor cold flow behaviour. Using additives, these disadvantages can be eliminated. Manufacturers of different vegetable oils can use the same base stock for each formulation, but they may pick different additives to adapt the final product to the needs of a particular application. Common additives include those that delay or prevent oxidation, detergents and dispersants that improve efficiency, extend the lubricant's lifespan, and ensure cleanliness, viscosity modifiers that maintain viscosity over a wider range of temperatures, corrosion inhibitors that protect metal from oxygen, water, acid, base, and salt attacks, pour point depressants that prevent the formation of large crystals during solidification, and anti-wear additives. It is normal practice to employ additives when creating lubricants; nevertheless, it is imperative that petroleum-based compounds currently in use, such as ZDDP, be replaced with chemicals that are less harmful to the environment. For instance, research is being conducted to discover if ethyl cellulose can be utilized in high oleic sunflower (HOSO) and castor (CO) oils as an environmentally friendly, multifunctional additive. It has advantages such as a wider range of operating conditions under which fluid film lubrication can be maintained, a wider range of kinematic viscosity, and a better viscosity temperature dependence than many mineral or synthetic oil lubricants, making it suitable for a wide variety of lubricant applications (Naole, n.d.).

## 2.5 Additives

Lubricating oils have been improved by the use of additives. These additives include anti-wear, extreme pressure, viscosity control, film-forming, and deposit control. In recent years, nanoparticles have attracted a significant lot of interest because to their unique properties in comparison to their bulk counterparts. It has been proved that using nanoparticles as additives reduces friction and wear. By adding SiO<sub>2</sub> and diamond nanoparticles to liquid paraffin, friction was minimized compared to liquid paraffin oil with no additives. Because the nanoparticles operated as load-bearing components, the incorporation of ZnO, CuO, and ZrO<sub>2</sub> into polyalphaolefin decreased friction and wear. Several lubrication mechanisms, such as the repairing effect, the spinning effect, the refining effect, and the insulating film, have been advanced to explain the role of nanoparticles in diesel fuel. Although it has been demonstrated that nanoparticles improve lubricant properties, compatibility is now a concern. Over time, nanoparticles tend to settle, altering the consistency of the lubricant. The formulation of a stable suspension is a crucial issue in nano-lubrication due to the production of sediments and agglomerates due to a lubricant's less stable suspension over a long period of time in static environments (Cortes et al., 2020).

In recent years, nano lubrication has helped to the growth of the tribology sector. Nano lubricants are the dispersion of nanoparticles in a base oil; their prospective applications have piqued the interest of researchers. Nanoparticles are utilized in the medical, space, and materials industries, in addition to tribology. Nanoparticle addition to base oils is promising since it enhances specific tribological properties, such as wear-resistance and friction, and the majority of them are environmentally friendly. Numerous studies have documented the numerous nanoparticles (NPs) used as lubricant additives; vegetable oils, metallic, ceramic,

composite, natural, and synthetic NPs all exhibit superior wear and friction reduction (Ali et al., 2021).

## **2.6 Differential Scanning Calorimeter (DSC)**

For the purpose of determining the thermal property of the membrane, a differential scanning calorimeter is utilized (Mettler Toledo DSC 822e). Until it reaches a temperature of 250 degrees Celsius, the temperature of the sample will be raised at a rate of 10 degrees Celsius per minute. The starting point ( $T_g$ ) for the calculation of the temperature of the glass was found by taking the point of intersection of the slopes (Gama, 2020).

The measurement of thermodynamic changes in a substance induced by chemical reactions, phase shifts, and other physical changes is called calorimetry. Samples of nanoparticles are amenable to being analyzed with a wide variety of calorimetric techniques. The differential scanning calorimeter (DSC) is capable of measuring both thermodynamic data (heat capacity, enthalpy, and entropy) and kinetic data (reaction rates, activation energies). The difference in heat flow between the sample (TS) and a reference material (TR) is monitored and recorded as a function of the temperature. The sample cell and the reference cell in a DSC are heated separately in such a way that  $DT14TS-TR140$ , and the heat flow differential is recorded as a function of temperature. In the event that a substance goes through either an endothermic or an exothermic phase transition, the quantity of heat that is necessary to keep the sample at the same temperature will either grow or decrease proportionally. The difference in the amount of energy needed to bring the sample temperature up to the reference level corresponds to the amount of surplus heat that is generated or absorbed as a result of sample transitions (Mansfield, 2015).

## **2.7 Rheological Measurements**

Using a commercial rheometer called the HAAKE RS-150 RheoStress (Haake Instruments, Inc., Paramus, NJ, USA) with double parallel plates spindle, SiO<sub>2</sub> and TiO<sub>2</sub> nanoparticles dispersed in sunflower oil were characterized rheological. The distance between the upper and bottom plates was half a millimeter. In order to carry out the analysis, 0.9 mL of the sample being tested was utilized. The combination of sunflower oil and nanoparticles can be classified as either a colloidal suspension or a non-Newtonian fluid with shear-thinning or thickening properties. This determination is made based on the size of the nanoparticles. During the course of the rheological characterization, which took place at a temperature of 22 degrees Celsius, the measurements were taken. Shear rates ranging from 10 to 120 s<sup>-1</sup> were used to determine the viscosity of each and every sample, as well as the shear stress (Cortes et al., 2020).

## **2.8 Tribology test**

The standard ball test material was 52100 grade 25 chrome alloy steel with a 12.7 mm diameter, 0.1 μm surface roughness, 25 extra polishes (EP), and 54–58 HRC hardness. Each test utilized four brand-new balls. Each time before beginning a new test, the balls were cleaned with a technical cleaner (isoparaffin-based solvent cleaner) and dried with tissues. 52100 steel is extensively used in the industrial and automotive sectors for ball and roller bearings. It is renowned for its outstanding surface quality, wear resistance, hardness, and weight carrying capacity (Birleanu et al., 2022).

## CHAPTER 3

### METHODOLOGY

#### 3.1 Lubricating preparation

In this research project, 5 lubricants including synthetic lubricant and vegetable oils are used. The Titanium Dioxide (TiO<sub>2</sub>) additives are mixed into the vegetable oils.

##### 3.2.1 Synthetic lubricant

Synthetic lubricant SAE5W40 is used to be compared to vegetables oils that is added additive to them. The synthetic lubricant is purchased at petrol station. The Appendices contain a listing of the technical specifications. This synthetic lubricant is utilized for usage in automobiles, including luxury automobiles. Figure 3.1 shows the type of synthetic oil chosen for this experiment.

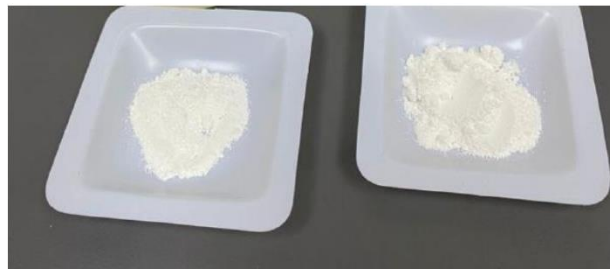


*Figure 3.1: Synthetic Lubricant SAE5W40*



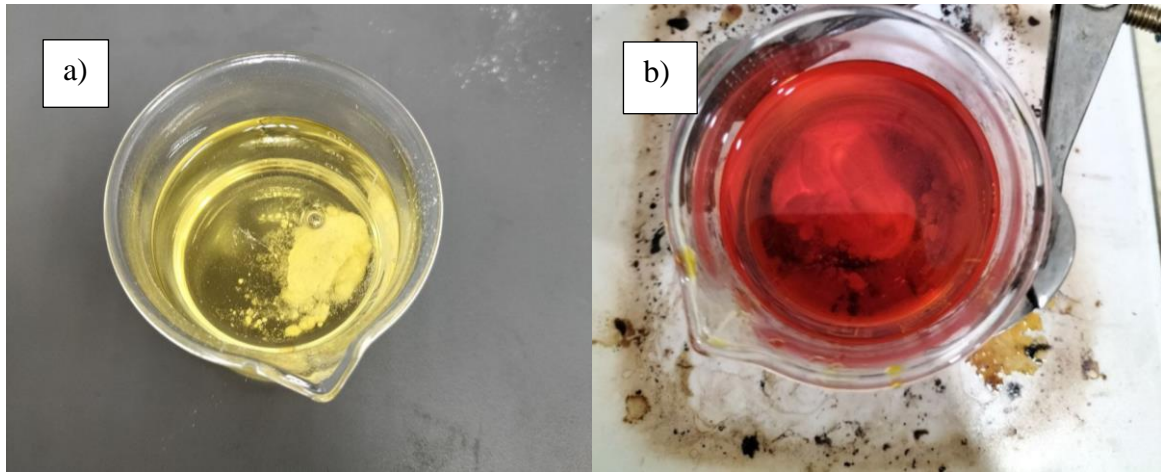
### 3.2.2 Vegetable oils with TiO<sub>2</sub> additives

Vegetable oils are used such as red palm oil, soybean oil, sunflower oil, and coconut oil. The vegetable oils and TiO<sub>2</sub> particle are obtained from online supplier. The synthesis of the bio-lubricant utilizing TiO<sub>2</sub> nanoparticles was accomplished using a method that only required one step. The one-step approach consists of immediately mixing the nanoparticles with the base oil in a single step. To distribute the nanoparticle throughout the base oil, sonication and stirring were utilized. Figure 3.2 shows the nanoparticles used which are in the form of powder.



*Figure 3.2: TiO<sub>2</sub> powder*

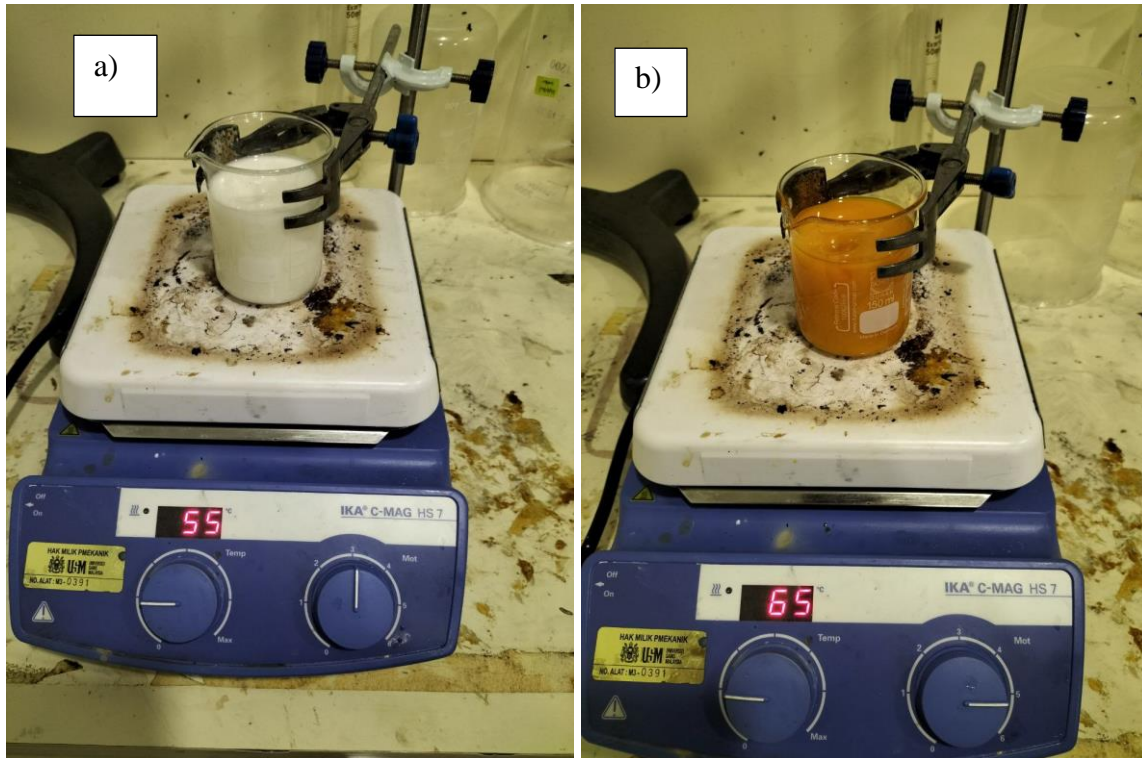
In this research project, the bio-lubricants are added with 1wt% concentration of TiO<sub>2</sub>. Firstly, the additives of 1.2g are weighed using a digital weight scale for 120ml of bio-lubricant. Then, the nanoparticles were poured into a beaker containing 118.8ml of bio-lubricants as shown in Figure 3.3. Next, Figure 3.4 shows the process of sonication are be carried out on the solution for close to half an hour, with intervals of ten minutes of operation followed by five minutes of rest. It is because to maintain the physical properties of the base oil. After that, by using a magnetic stirring machine, the base oil combined with TiO<sub>2</sub> is swirled for ten minutes. Figure 3.5 shows the process of stirring of vegetable oils with TiO<sub>2</sub> additives.



*Figure 3.3: TiO<sub>2</sub> additives in bio-lubricants before mix together (a) Soybean oil (b) Red palm oil*



*Figure 3.4: Sonication process for red palm oil after added TiO<sub>2</sub>*



*Figure 3.5: Stirring process for to ensure proper solution to ensure proper solution mixing (a) Soybean oil (b) Red palm oil*

### 3.3 Rheological Measurements

The Rheometer is used to measure the rheological properties of the solution of vegetable oils TiO<sub>2</sub> additives. The rheological properties of lubricants are significant to the ultimate use and to their general effectiveness. This indicates that, during a viscosity measurement, the rheometer presets a current that corresponds to predetermined rotational speed, revolutions per minute (rpm) and temperature. Figure 3.6 shows the viscosity meter used to measure torque, shear stress, viscosity, and shear rate. All the setting of program are done by pressing the keypad on the DV-III ULTRA Programmable Rheometer panel as shown in Figure 3.7.



Figure 3.6: Viscosity Meter Brookfield



Figure 3.7: Program panel of Viscosity meter

Firstly, the instrument is switched on. Then, the button of ‘Motor On/Off’ is set to autozero as shown in Figure 3.8. After that, the sample is poured into the sample port and tighten the handle screws. Figure 3.9 shows the sample of red palm oil in the sample port. The appropriate spindle is selected and then, the ‘no of spindle’ is entered by pressing the number on the panel. the temperature and rpm are set before running the test. The test is run by pressing the button of ‘Motor On/Off’. After a few seconds, the data are obtained and the ‘Select DISP’ button is pressed to get those data. Then, the sample holder is washed and dried with tissues before changing other samples. The samples used are all vegetable oils with TiO<sub>2</sub> additive and synthetic lubricant. The sample holder and spindle are cleaned before shutting down and put them inside their case. Lastly, switched off the instrument. This experiment is done in two different temperatures which are 60°C and 27°C. Hence, six different of rpm are used in this experiment which are 50, 80, 100, 120, 150 and 200. Figure 3.10 shows the water bath is set at 60°C and switched on it along the experiment. For 27°C, the water bath is switched off to remain the room temperature.



*Figure 3.8: Ensure the screen display is autozero before setting any program*



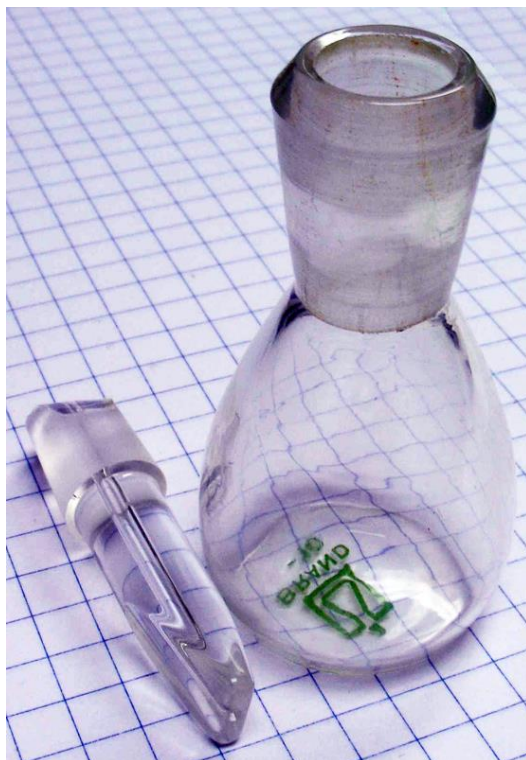
*Figure 3.9: Red palm oil with TiO<sub>2</sub> additives in sample port*



*Figure 3.10: Temperature setting of water bath*

### 3.4 Density Test

The pycnometer, also known as specific gravity, is a flask with a close-fitting ground glass stopper with a small hole through it, allowing for the accurate measurement of a given volume. This allows the density of a fluid to be reliably evaluated using an analytical balance and a suitable working fluid such as water or mercury. Figure below shows the pycnometer used in the experiment (*Designation: D 1481-02 Standard Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Lipkin Bicapillary Pycnometer 1, n.d.*).



*Figure 3.11: Pycnometer*

The glassware is cleaned with soap and water and then rinsed with a small amount of acetone. Next, the flask and stopper are dried, then weighed them on the analytical balance. The exact volume of the pycnometer is determined by filling it fully with the lubricant, inserted

the stopper, and tapped the sides gently to remove the air bubbles. After that, the sides are dried, and the pycnometer is weighed on the analytical balance. The temperature of water is measured. The volume of lubricant contained in the full pycnometer flask is determined. The samples used are all vegetable oils with TiO<sub>2</sub> additive and synthetic lubricant.

### **3.5 Differential Scanning Calorimeter (DSC) Test**

The differential scanning calorimeter, or DSC, can be used to estimate the melting and mesomorphic transitions, as well as their respective entropy and enthalpy values. Hence, DSC is used to measure the thermal property of the membrane by using a combination of heating and cooling to create a heat flow graph.

For machine set up, the Tzero Hermetic lid and Tzero low-mass pan are used as the lubricant holder. Then a small portion of lubricant is loaded into the bottom of the pan. The pan contain of lubricant is weighed using digital weight scale. After that, the lid is placed concave down and fit snugly into the pan. The pan is placed on the lower die set. The upper die and lower die set are placed into the press. Afterward, the handle is lowered to seal the pan. Then, the sample is placed into the DSC machine. Figure 3.12 shows the apparatus are used to prepare the sample for this experiment.



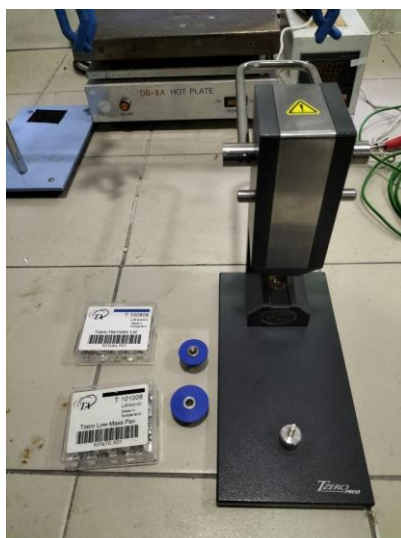


Figure 3.12: Tzero Hermetic lid and pan, blue die set and sealing press

Before running the test, the program is set up. Figure 3.13 shows the part of program set up. The program is set to cooling, then heating process. After that, the liquid nitrogen is poured into the DSC machine during the cooling process as shown in Figure 3.14. The liquid nitrogen is to speed up the cooling process. For heat process, the DSC machine is covered. Figure 3.15 shows the sample is underwent the heat process. The samples used are all vegetable oils with TiO<sub>2</sub> additive and synthetic lubricant.

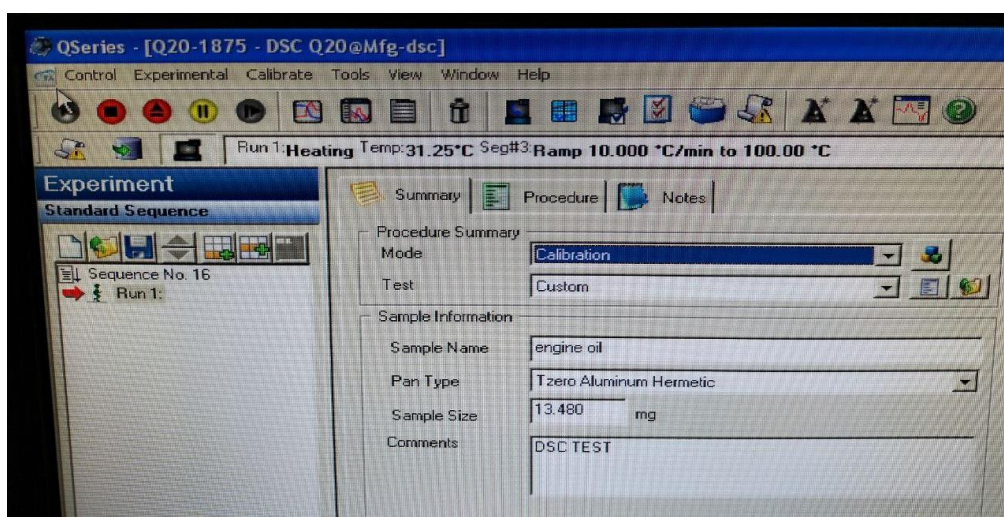


Figure 3.13: DSC program set up



*Figure 3.14: Cooling process during DSC analysis running*



*Figure 3.15: Heating process during DSC analysis running*