ANALYSIS OF ADDITIVES FOR BIO-BASED ENGINE OIL FOR A TWO STROKE MARINE ENGINE

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FACULTY OF ENGINEERING
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THESIS SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MECHANICAL ENGINEERING

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Abstract

Bio-based oil synthesis through Neopentyl glycol (NPG) and Trimethylolpropane (TMP) ester are used to produce biodegradable bio-lubricant for a two stroke marine engine. Two stroke engine, specifically for marine activities, widely uses synthetic lubricant in the fuel-oil mixture as it is easily available and at low cost. This has huge impact to the environment as two-stroke marine engine release its byproduct directly into the aquatic environment during its operation and the less stringent law encourage this to occur widely around the world. Bio-based oil with the combination of Group II synthetic oil with various composition allow us to find the optimum composition to produce the similar or better performance of fuel-oil mixture compared to using synthetic oil entirely. Additives of Graphene Oxide (GO), Anti-Oxidant (AO), PIB and solvent are added into this bio-based oil mixture to enhance its performance and capability of using bio-based oil. The physicochemical properties of viscosity, density and VI ratio are obtained through advance viscometer. Sample with 50% bio-based oil and 50% Group II mineral oil has the most optimum result among the tested composition, including the baseline reference lubricant suggested by the two-stroke marine engine manufacturer. An improvement of 28.36% when compared to the baseline sample in terms of Viscosity Index (VI) is observed, whereby Sample 3 has VI value of 160.4. The higher VI allow it to operate at various temperature range which is a key factor marine use as the environment varied throughout the day. Through the wear scar diameter test and obtaining the coefficient of friction, the bio-based oil alone has outrun the synthetic oil, both from Group I and Group II base oil. This factor is critical to ensure engine lubrication of bio-based oil is on par or perform even better for engine performance. Each sample of bio-based oil mixture is tested in actual two-stroke marine engine to find out the deposition of carbon on the spark plug. Sample with bio-based oil from PNAF-NPG ester shows the most optimum result with the least amount of carbon deposition on the spark plug and at dry condition for moisture rating. Whereas for TMP ester, composition of this bio-based oil that is more than 30% will cause carbon to deposition on the spark plug – however the moisture rating remained low. Complex microstructure of TMP required higher temperature during combustion process to completely process all the TMP. Hence, TM would be useful to be used on engine with higher revolutions. The similar result is observed when using a lower revolution two-stroke engine. As such, the usage of bio-based oil from PNAF-NPG is acceptable and able to provide satisfactory results on low or high revolution two-stroke engine.

Keywords: **lubricant, engine oil, two-stroke engine, marine**

Abstrak

Sintesis minyak berasaskan-bio melalui Neopentyl glycol (NPG) dan Trimethylolpropane (TMP) ester digunakan untuk menghasilkan pelincir biodegradasi untuk enjin dua jelang. Enjin dua lejang, khusus untuk aktiviti laut, menggunakan pelincir sintetik secara meluas dalam campuran bahan bakar-minyak kerana mudah didapati dan dengan kos rendah. Ini memberi kesan besar kepada alam sekitar kerana mesin marin dua lejang melepaskan produk sampingannya terus ke persekitaran air semasa pengoperasiannya dan undang-undang yang kurang ketat mendorong ini berlaku secara meluas di seluruh dunia. Minyak berasaskan-bio dengan gabungan minyak sintetik Kumpulan II dengan pelbagai komposisi membolehkan kita mencari komposisi optimum untuk menghasilkan prestasi campuran minyak-minyak yang serupa atau lebih baik berbanding dengan menggunakan minyak sintetik sepenuhnya. Bahan tambah atau aditif *Graphene Oxide* (GO), Anti-Oksidan (AO), *PIB* dan pelarut ditambahkan ke dalam campuran minyak berasaskan-bio untuk meningkatkan prestasi dan keupayaannya menggunakan minyak berasaskan-bio. Sifat fizikokimia kelikatan, ketumpatan dan VI diperoleh melalui viskometer. Sampel dengan 50% minyak berasaskan-bio dan 50% minyak mineral Kumpulan II mempunyai hasil yang paling optimum di antara komposisi yang diuji, termasuk pelincir rujukan asas yang dicadangkan oleh pengeluar mesin marin dua lejang. Peningkatan sebanyak 28.36% jika dibandingkan dengan sampel asas dari segi *Viscosity Index* (VI) dapat diperhatikan, dimana Sampel 3 mempunyai jumlah VI sebanyak 160.4. VI yang lebih tinggi membolehkannya beroperasi pada pelbagai suhu enjin yang merupakan faktor utama penggunaan laut kerana persekitarannya berubah sepanjang hari. Melalui ujian diameter bekas luka dan memperoleh pekali geseran, minyak berasaskan-bio sahaja telah mengatasi minyak sintetik, baik dari minyak asas Kumpulan I dan Kumpulan II. Faktor ini sangat penting untuk memastikan pelinciran enjin minyak berasaskan-bio setara atau lebih baik untuk prestasi enjin. Setiap sampel campuran minyak berasaskan-bio diuji dalam mesin marin dua lejang untuk mengetahui pemendapan karbon pada busi. Sampel dengan minyak berasaskan-bio dari ester PNAF-NPG menunjukkan hasil yang paling optimum dengan pemendapan karbon paling sedikit pada palam pencucuh dan pada keadaan kering untuk penilaian kelembapan. Manakala bagi ester TMP, komposisi minyak berasaskan bio ini yang melebihi 30% akan menyebabkan karbon terendap pada palam pencucuh - namun kadar kelembapannya tetap rendah. Struktur mikro kompleks TMP memerlukan suhu yang lebih tinggi semasa proses pembakaran untuk memproses semua TMP sepenuhnya. Oleh itu, TMP akan berguna untuk digunakan pada mesin dengan revolusi yang lebih tinggi. Hasil yang serupa diperhatikan ketika menggunakan mesin dua lejang revolusi bawah. Oleh itu, penggunaan minyak berasaskan-bio dari PNAF-NPG dapat diterima dan dapat memberikan hasil yang memuaskan pada mesin dua lejang revolusi rendah atau tinggi.

Keywords: **pelincir, minyak enjin, enjin dua jelang, marin**

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LIST OF SYMBOLS AND ABBREVIATIONS

2T	:	Two Stroke
AM2	:	Aryl-Amine Antioxidant
AO	:	Anti-Oxidant
API	:	American Petroleum Institute
ASTM	:	American Society for Testing and Materials
DFI	:	Direct Fuel Injection
DLTDP	:	Sulfur-containing Auxiliary Antioxidant
GO	:	Graphene Oxide
HC	:	Hydrocarbon
IMA	:	International Maritime Organisation
NOx	:	Nitrogen Oxide
NPG	:	Neopentyl glycol
PET	:	Pentaerythritol
PFAD	:	Palm Fatty- Acid Distillate
PIB	:	Polyisobutylene
TBHQ	:	Tert-Butyl Hydroquinone
TMPO	:	Trimethyl Propane Trioleate
VI	:	Viscosity Index

CHAPTER 1: INTRODUCTION

1.1 Background

Marine transportation activities are the major contributor to both air pollution and marine pollution. A large number of marine engine, especially outboard two stroke engine, is one of the contributor to marine pollution whereby large amount of toxic material is directly release into the marine environment from the engine as by-product. For a two stroke marine engine, fuel and oil are mixed and undergo combustion together, before the excess is being released together with the by-product (exhaust) into the external environment (C. Kelly, Brown, Rea, Scott, & Hargreaves, 2001).

Since the commonly used engine oils are usually synthetic or mineral based, they are highly not biodegradable material. They are commonly used as they are cheap and widely available in the market, despite many of them are not in line with the regulation set by the International Maritime Organisation (IMO). This is largely due to the less stringent law applies to the fishermen community in South East Asia, whereby there are a significant portion of the local economy is from marine activities.

The use of bio-based engine oil mixture has proven to be a success to form a good mixture with synthetic or mineral oil in terms of the physiochemical and tribological behavior. Bio-based engine oil has significantly good biodegradable property, hence it safer to be used for marine activity.

However, to suit the bio-based engine oil mixture to have similar or better performance compared to the mineral oil, optimum composition between bio-based oil and mineral oil have to be considered. The additives function such as to prevent rust and corrosion, gives optimum oil viscosity for wear protection, and control the by-product such as Sulphur Dioxide production or carbon deposition (D. Wu et al., 2018).

Through this research, a selection of carefully measured additives will be added into a premixed base oil and fuel mixture and the outcome will be analyses to find out the suitable additives for the above functions. Composition between bio-based oil and mineral oil will be considered carefully to ensure optimum composition will be found.

The tribology properties of mixture will be analyses with the appropriate tool to find out the effectiveness of the added additives. To determine the functionality of the additives on wear and rust protection and by-product analysis, a set of experiment and study will be ran with a two stroke marine engine to mimic an outboard marine engine that is commonly used by the fishermen community. Condition of the engine spark plug will be examine after each run to determine the result.

Through these processes and analyses, an optimum composition mixture can be determined and being used as the formula to produce the optimum bio-based oil mixture for a two stroke marine engine.

1.2 Problem Statement

By-product of combustion on a two stroke marine engine produce and release a certain amount of pollutant that is harmful to the aquatic life. A two stroke engine has the tendency to release approximately 30% of the fuel and oil mixture at every cycle. Current marine engine oils used in the market are mostly synthetic or mineral-based, where it is not biodegradable upon release to the marine environment and thus further polluting the environment (Di Natale et al., 2013).

Bio-based oil alone will not able to achieve the similar performance of what mineral oil can do. Finding the optimum composition mixture between both of these engine oil is required to ensure equivalent or better performance will be achieve while not neglecting the impact to the environment.

Since any by-product from the combustion of bio-based and fuel mixture will be release directly to the marine environment, this will prone to aquatic pollution. Hence, to produce a proper marine engine oil from bio-based material, certain additives are added into the engine oil to ensure it will be suitable for marine condition. The additives function such as to prevent rust and corrosion, gives optimum oil viscosity for wear protection, and control the by-product for Sulphur Dioxide production as by-product.

The additives added into the engine oil should not compromise the performance of the engine by a large factor. Certain trade-off between performance and emission should be considered

1.3 Objectives

1) To evaluate the physiological properties of different composition of bio-based oil to mineral oil used in a two-stroke marine outboard engine.
2) To investigate the effect of adding bio-based oils on spark plug carbon deposition using two stroke marine outboard engine.
3) To study the difference of engine operating at high and low revolutions towards spark plug carbon deposition with the presence of bio-based oils.

1.4 Contributions

The contribution of the research is to reduce the environmental impact to the marine life by utilizing biodegradable bio-based lubricant as one of the major component in producing engine oil mixture while retaining its performance of engine oil as required by the manufacturer. Throughout the study, the optimum composition between bio-based oil and mineral oil can be obtained successfully.

1.5 Scope of Research

The purpose of this study is to determine the tribological and physiochemical properties of bio-based oil mixture using PFAD-NPG ester and TMP ester in combination with Type II mineral oil. Lubricant additives comprised of Graphene Oxide, Anti-Oxidant, PIB 1300, PIB 1100 and Solvent are added to improve the quality of the bio-based oil used in this study. The tribological and physiochemical properties of the samples are examined through four ball tester and viscometer, respectively. Samples with different compositions of bio-based oil and mineral oil are tested with actual two-stroke marine engine.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

A number of researches have been carried out that covered the topic of the relationship between lubricant and engine, as well as their impact towards the environment. A large number of the researches are focused on the four-stroke engine as its commercial impact is higher and being used by larger organization. However, a larger number of two stroke engine transportations are still widely used in many places and it gives a larger impact towards the environment. There are researches that have been done to utilize bio-based lubricant to achieve similar or better performance to a mineral oil or synthetic oil – in addition of additives compound to improve the bio-based lubricant physiochemical properties and tribological properties. Apart from engine performance, the impact of bio-based lubricant towards the marine environment is also being looked into detailed by several researchers as in an operating condition of a two stroke engine, the fuel and lubricant are mixed and feed into the combustion chamber in a form of mixture. Unburnt fuel and lubricant are directly release into the marine environment through the exhaust port. This is also true to any form of by-product from the combustion of the mixture.

2.2 Two-Stroke Marine Engine

Maritime transport is the main source of pollution to the marine life as majority of the marine engine by-product is not treated properly before releasing to the marine environment mainly due to majority of the shipping routes have minimal emission control. The pollutants are mainly greenhouse gases, Sulphur dioxide, transition metals, and soot (Sippula et al., 2014). Overall, the combined marine engine usage in the world produce more Nitrogen oxide pollutants compared to land transportation. To make matter worse, marine sector is not being regulated until the 90s – comparative to land transportation (Di Natale et al., 2013). As shown in Figure 2.1, the cross-sectional of a typical two stroke engine – whereby the fuel and lubricant pre-mixture is feed into the combustion chamber together for combustion process.

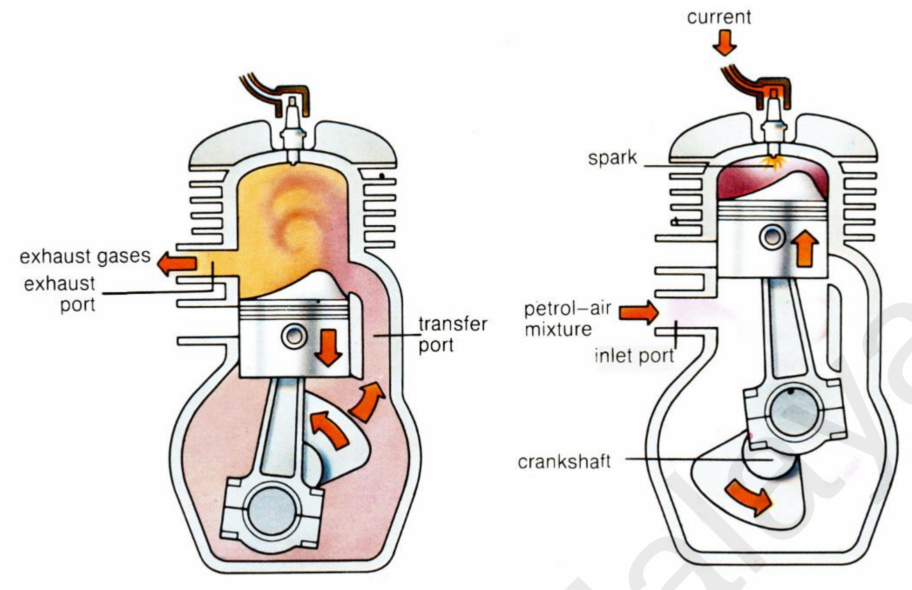


Figure 2.1: Schematic cross-sectional diagram of a typical two-stroke engine.

Unlike four-stroke engine, two-stroke engine do not have oil sump to store lubricant and recycle lubricant during the operation of the engine. Lubricant is mixed into the fuel and thru combustion process – they are burn and release into the environment – in this case which is the marine environment.

2.3 Pollutions from Marine Activities

In a two-stroke engine operation, fuel-lubricant mixture that is left unburnt during combustion process and its by-product are directly release into the marine environment. Various harmful substances are added into the marine environment such as toxic hydrocarbons, nitrogen oxides, Sulphur, volatile organic compounds (VOCs) and various number of compounds. Water quality is also badly affected due to the particulate matters and carbon deposition – resulting in murky and a dirty water that would eventually affect the food chain in the area due to migration or threat to the marine life. These pollutants does not clear up in short period of time, in fact it will last up to 2 weeks in the zone before slowly disperse away. Studies show that comparing between modern marine transportation with older generation land transportation, the former produces pollutants at much higher magnitude at the same duration of use (Martin, 1999).

Due to pressure from international mandate, modern engineering is attempting to reduce this by implementing advance engine design to reduce the pollutions like developing direct fuel injection (DFI) engine into a two stroke engine. This technology existed for quite some time however it is not implement into a two stroke engine until recent years. Via a DFI, the fuel is injected directly at the combustion chamber at the right timing of each stroke – whereby the exhaust and intake valves have closed preventing excretion of fuel mixture. Hence, only small amount of lubricant is required to lubricate the piston and other moving parts in the two stroke engine – instead of mixing it into the fuel (C. A. Kelly, Ayoko, Brown, & Swaroop, 2005). Figure 2.2 shows the example of DFI feature in a two stroke engine, whereby the lubricant is separated from the fuel mixture and the fuel is inserted directly on the combustion area. This could drastically reduce the emission of unburnt lubricant while retaining the performance of what two stroke engine could produce.

With current technology and properly selected additives, various bio-based lubricant can be used to replace the toxic synthetic lubricant being used widely commercially. Through this study, an optimum selection of bio-based lubricant will be selected to replace the recommend synthetic lubricant suggested by the manufacturer of a two stroke engine – without sacrificing its performance.

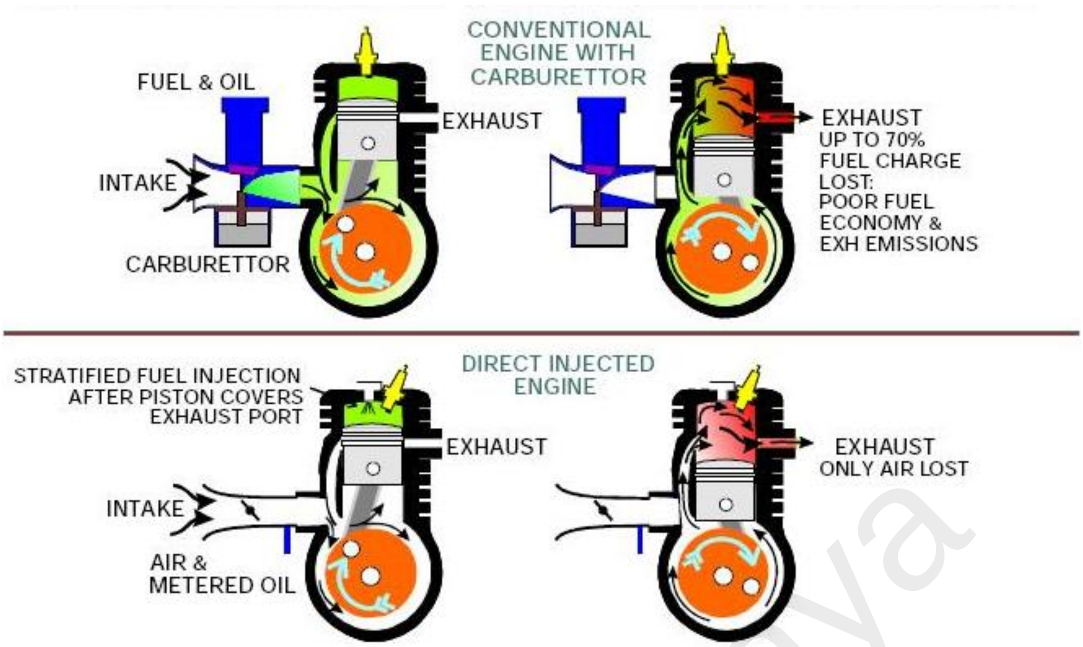


Figure 2.2: Example of direct fuel injection in a two stroke engine.

2.4 Mineral Oil & Synthetic Oil

To have a good balance between economical reason and engine performance, a large number of users operating two stroke engine are using non-bio-based oil for lubricant and rather to go for the commercial mineral oil, semi-synthetic oil or fully synthetic oil. Despite being produced from natural content – mineral oil is still toxic to be release directly into the marine environment without being treated properly. As for semi-synthetic oil is the combination between mineral oil and engineered synthetic oil whereby its performance is relatively acceptable by various applications as it is classified as Group II under API. Group II based-oil is able to achieve viscosity index more than 120 and low amount of Sulphur, at no more than 0.03%. Synthetic oil is produced chemically by synthesizing based-oil without any mineral oil in its content – this is the most reliable based oil in terms of engine performance however as being fully synthetic, it is not possible to be biodegradable and extremely harmful to be release directly into the marine environment (Adhvaryu, Erhan, Sahoo, & Singh, 2002).

2.5 Biodiesel Oil – NPG & TMPO

Various biodiesel oil or bio-lubricant can be used as the base oil of the engine oil mixture. A process of enzymatic synthesis is used to produce the bio-lubricant using biodegradable raw material. For instance, soy bean and castor bean are commonly used for this process. The widely available synthetic oleo-chemical esters are trimethylolpropane (TMPO), neopentyl glycol (NPG) or pentaerythritol (PET). (Aguieiras et al., 2020). Figure 2.3 and Figure 2.4 shows the 3D molecular structure of bio-based ester of TMPO and NPG, respectively.

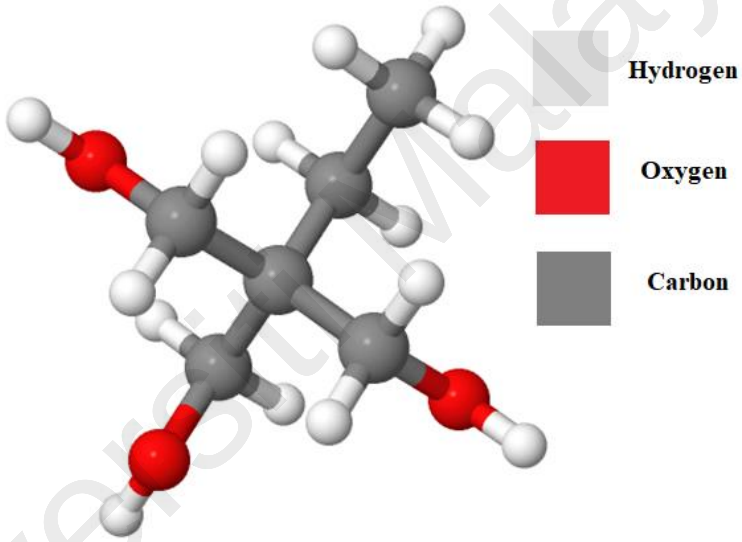


Figure 2.3: 3D molecular structure of TMPO.

These esters have lower pour points than the original oil and retain biodegradability and lubrication characteristics of the natural oil. (Yunus et al., 2004). TMP ester is able to achieve lower its pour points by optimizing its fatty acid composition and reaction conversion – thus achieving the pour points temperature of at least -32 C. This is crucial for lubricant manufacturer as bio-based esters tends to give poor low temperature properties unless additives are added. However, certain additives will give drawbacks to the original performance of bio-based ester lubricant (Yunus, Fakhru'l-Razi, Ooi, Omar, & Idris, 2005).

Apart from this, bio-based ester lubricant tends to have poor oxidative stability if it is used in its natural-state without any additives component. Researches are done to study the most optimum additives that suitable for high temperature operation like a marine engine with high revolution. It is found out that aryl-amine antioxidant (Am2) provides the most optimum result in terms of oxidation stability and retaining lubricant performance in high temperature. The performance of this antioxidant further elevates if the synergies of Am2 and a sulfur-containing auxiliary antioxidant (DLTDP) in done prior to combining with the TMP bio-based ester lubricant (Y. Wu, Li, Zhang, & Wang, 2013). TMP ester based lubricant does also provides good wear prevention when it is specified at amount of 7% of the total amount of ordinary lubricant (Zulkifli, Kalam, Masjuki, Shahabuddin, & Yunus, 2013). TMP could work well and give a good quality of combustion in a specific blend ratio as performed in previous study (Zulfattah et al., 2019). As in terms of engine performance, friction is something unavoidable and the presence of good wear prevention lubricant could extend the life of the marine engine and ultimately the performance of the engine.

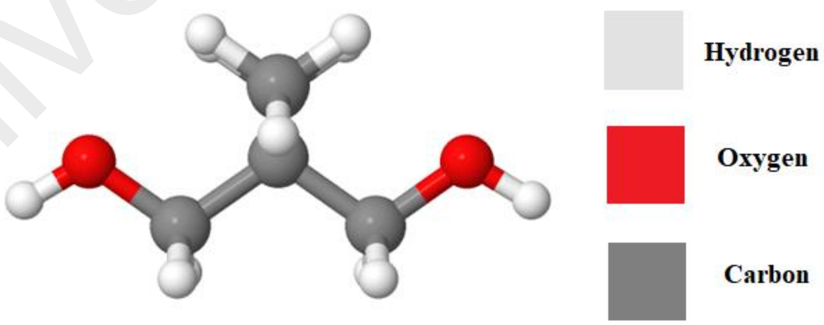


Figure 2.4: 3D molecular structure of NPG.

Multiple researches are performed on neopentyl glycol (NPG) ester lubricant as it gives relatively good results in terms of physio-chemical properties when compared to commonly use marine engine oil. NPG ester lubricant is shown to have high value of

Viscosity Index that could possibly match a Group III synthetic based oil whereby the VI value is above or equal to 120. As for wear prevention properties, NPG ester delivers the least wear rate comparative to other tested bio-based lubricant ester – accordance to ASTM D 4172 method. Its pour points are relatively low – at average of -22 C (Kamalakar, Sai Manoj, Prasad, & Karuna, 2015).

2.6 Compositions – Additives & Solvent

Biodiesel itself will not perform well in a marine engine as its own properties has the disadvantage of high viscosity, lower oxidation stability and lower volatility. With the combination of certain additives and solvents, these drawbacks can be resolved and biodiesel can be used widely. A package of additives and solvents are added into the biodiesel oil in the preparation of the biodiesel oil package. Graphene oxide is widely used to improve the lubrication properties of biodiesel oil as it formed a lubrication layer between steel/iron contacts. It creates a tribofilm layer – acting as a protective role and create an antifriction contact between steel/iron, in this case it is the piston and the piston wall of a marine engine (D. Wu et al., 2018). From the observation on Figure 2.5 is showing the presence of tribofilm in the setup, similar to what happened between the wall of cylinder and the actuating piston body.

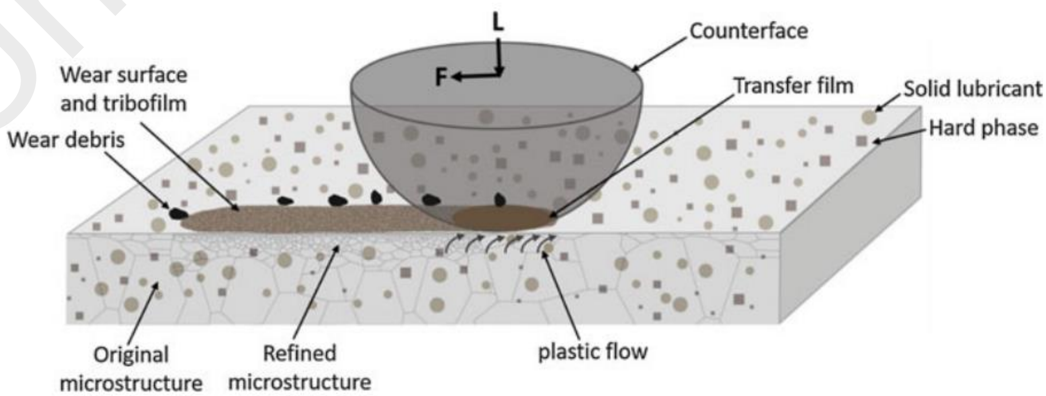


Figure 2.5: Example of tribofilm exist between two contact surface with the presence of lubricant.

As biodiesel oil is reported to produce a rather higher emission of Nitrogen oxide, the emission need to be controlled in a manner to prevent it become a significant draw back to not use biodiesel fuel as a replacement of petroleum fuel (Heidari, Najjar, Burnens, Awad, & Tazerout, 2018). Anti-oxidant is added into the additives package to control and reduce the emission of Nitrogen oxide during combustion. As there are various anti-oxidant can be used – certain anti-oxidant such as tert-butyl hydroquinone (TBHQ) is commonly used as it improve the storage stability of biodiesel fuel (Hess, Haas, Foglia, & Marmer, 2005).

To further improve biodiesel fuel usage, the by-product is reduced by introducing Polyisobutene or better known as PIB to reduce the smoke production after combustion of biodiesel fuel in the marine engine. This is useful to a two stroke engine whereby the PIB also act as attractant for dirt upon combustion (Waters & Waters, 2010) (Broun, Fog, & Gorland, 1989).

As biodiesel has higher viscosity level, it is required to lower this level to optimise the performance of an engine and subsequently reducing the pressure in the engine. Diluent is added as part of the additive package to improve the slickness of fuel mixture with biodiesel. Chlorinated diluent will perform well in such case, however since the untreated by-product of a marine engine is introduce directly into the marine environment – this is not practical step to take. As such, aromatic diluent is often use for this purpose and various commercial diluents offer such material – such as ExxSol D80 or ShellSol D80. With such solvent added, the flashing point of the fuel mixture will be reduced and such properties allow complete combustion to occur in the marine engine (Costa et al., 2016).

2.7 Summary

Two stroke engine had been widely in use since the early stage of modern transportation. Various researches have been done to improve a two stroke engine –

however it was more commercially focused to improve a four stroke engine as it used in transportation in larger scale. Improvement like direct fuel injection of a two stroke engine is proven to be beneficial in terms of performance and reducing its impact on the environment. This is done as more stringent law to protect the environment is applied as the pollution to the marine environment has slowly become larger scale as modern marine transportation getting more attention. Researches have been done to study the types of pollutants sourced from marine engine usage – namely hydrocarbon, unburnt fuel, and sulphur and nitrogen oxide. In terms of quality of water, carbon oxides and particulate matters are directly impacting it. Mineral oil and synthetic oil are able to provide top of the line performance however its impact to the marine environment needs to be considered as well. For a two-stroke engine application, the by-product from its combustion is directly release into the marine environment as study shows. Bio-based oil derive from palm oil – namely NPG and TMP esters are able to produce equivalent performance of mineral oil and synthetic oil. This has been well proven through researches. With the aid of correctly used additives and solvent, there is high possibility that bio-based oil could one day replace the used of non-biodegradable oil / lubricant. However, a correct balance between the composition of bio-based oil and mineral oil is crucial as bio-based oil alone is not able to fully replace the performance of mineral oil and synthetic oil. This study is currently focused on evaluating the optimum composition between bio-based oil and Group II oil to be used on a marine grade two stroke engine.

CHAPTER 3: METHODOLOGY

3.1 Introduction

Performance of the bio-based lubricant and fuel mixture are tested and examined using a two-stroke marine outboard engine. The performance of the bio-based lubricant is measured via the observation of carbon deposition on the spark plug. The tribological properties of different formulation of bio-based lubricant mixture are examine in detailed via four-ball tribo-tester.

In reference to flow chart in Figure 3.1, the bio-based lubricant and fuel mixture is prepared with based oil, solvent and additives before mixing it with fuel to run in a two-stroke marine outboard engine. The based oil is prepared with multiple samples with different formulation and ratio between bio-based lubricant and commercial mineral lubricant to find out the most suitable formulation. Additive package and solvent are kept at constant ratio for all the samples.

The physiochemical properties of different formulation of bio-based lubricant mixture samples are tested using a certified viscometer and its value is compare against the baseline sample (two stroke engine manufacturer recommended lubricants) to ensure the value is equal or higher than it.

Fuel and lubricant mixture used in the setup is fixed at 40:1 as this is the most optimum fuel and oil mixture to give the best performance for a two-stroke marine outboard engine. The engine will be running until the fuel mixture is run out in the fuel tank on each sample. At the engine of every samples run, the spark plug will be removed and examined. Water sample where the marine outboard engine run is collected for further examination to determine the contaminants released into the water through the exhaust port. A new spark plug will before a new sample run begin and repeats the process again until all the samples are fully tested.

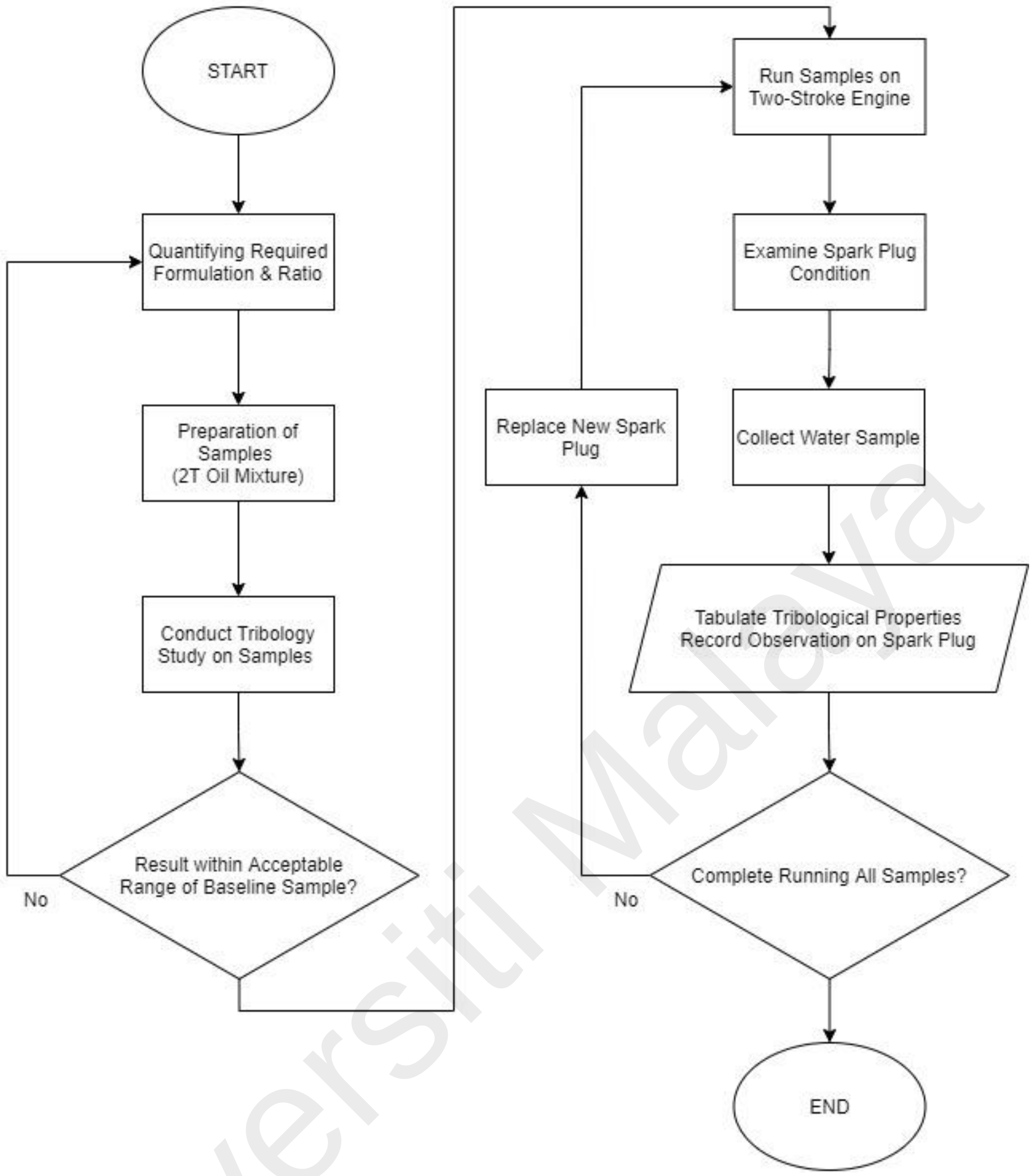


Figure 3.1: Flow chart to conduct and data collection of experiment.

3.2 Composition of 2T Oil Mixture

The 2T Oil Mixture consist of base oil mixture, solvent and additive package. A total of 6 samples of this mixture are prepared with different composition or ratio to suit the amount of fuel of 1000 ml. The amount of mixture of each sample is then calculated based on the fuel to lubricant ratio of 40:1 – this is the most optimum ratio for a two-stroke engine and as per recommended in the baseline sample engine oil.

3.2.1 Additives Package

A number of additives are added into the 2T Oil Mixture to enhance and improve the performance of the lubricant when reacted with fuel during the combustion in the two-stroke engine.

To reduce the friction in the engine during movement of the piston, graphene oxide (GO) is added to create a layer of film and optimize the movement between piston and the cylinder – thus improve the friction overall. This is crucial for the longevity and durability of the combustion chamber in long term of usage. To control the oxidation of the lubricant – with the presence of large amount of hydrocarbon, anti-oxidant (AO) is added into the mixture as it will reduce the oxidation process. With heat and oxygen presence with hydrocarbon, the mixture will likely to oxidize rather quickly and hence drastically reduce the performance of the engine.

A certain amount of highly reactive Polyisobutene (PIB) is added into the mixture to reduce the smoke generation upon combustion and also helps to reduce oxidation process to be taken place. A mixture of PIB1300 and PIB1100 are added into the mixture for this purpose. These PIB are also responsible of thickening of lubricant.

3.2.2 Solvent

With the mixture at high viscosity, solvent required to be added to prevent sludge remaining after combustion. Bio-based lubricant itself has high flash point – adding solvent allow the flash point to be reduced and further enhance the performance of combustion occurred in the engine. ShellSol D80 solvent is used in for this process.

3.2.3 Base Oil

Bio-based base oil used in this study is Neopentyl Glycol Dioleate (NPGDO) ester and Trimethylolpropane Trioleate (TMPTO) ester, where they will be mixed with a portion of mineral oil obtained commercially. The formulation of the mixture between the bio-based base oils and commercial mineral oil is distributed as shown in Table 3.1.

3.3 Preparation of 2T Oil Mixture

The amount of material is prepared and separated into six individual samples as shown in Table 3.1. All of the components used are carefully weigh on an electronic scale as shown in Figure 3.3 to ensure its accuracy. To prepare the fuel to lubricant ratio of 40:1, an approximately total of 40 gram of lubricant mixture is prepared per sample.

Table 3.1: Amount of additives and solvent required in each sample.

Type of Additives or Solvent	**wt. (%)**	**wt. (g)**
(Solvent) D80N	30.00	12.00
Graphene Oxide	0.05	0.02
Anti-oxidant	1.00	0.40
PIB1300	20.00	8.00
PIB1100	20.00	8.00
Total Additives & Solvent Package	**71.05**	**28.42**
Total Base Oil Required	**28.95**	**11.58**

Approximately 12 grams of base oil required to be prepared in each sample of total 40 grams. Sample 1 to Sample 3 are derived from NPG bio-based oil, whereas Sample 4 to Sample 6 are derived from TMP bio-based oil – as shown in Table 3.2.

Table 3.2: Weightage distribution of bio-based oil and mineral oil in each sample.

Base Oil Sample(s)	wt. (%)	g	wt. (%)	g
	Bio-Based Oil		**Group II**	
Baseline Sample	0	0	100	12
	NPG		**Group II**	
Sample 1	30	3.6	70	8.4
Sample 2	40	4.8	60	7.2
Sample 3	50	6.0	50	6.0
	TMP		**Group II**	
Sample 4	30	3.6	70	8.4
Sample 5	40	4.8	60	7.2
Sample 6	50	6.0	50	6.0

Prior to begin the mixing process, both of the bio-based oils are heated up to prevent any sediment and coagulation formed at room temperature using a hot plate magnetic stirrer. Figure 3.2 shows the hot plate magnetic stirrer used in the preparation.

Figure 3.2: Magnetic stirrer hot plate used to mix all the components in the mixture.

Each of the material is measured using a tared electronic scale prior to mixing it into the sample using a hot plate magnetic stirrer. The magnetic stirrer is set at 60 degree Celsius and stirring at approximately 1100 RPM until the mixture is well mixed.

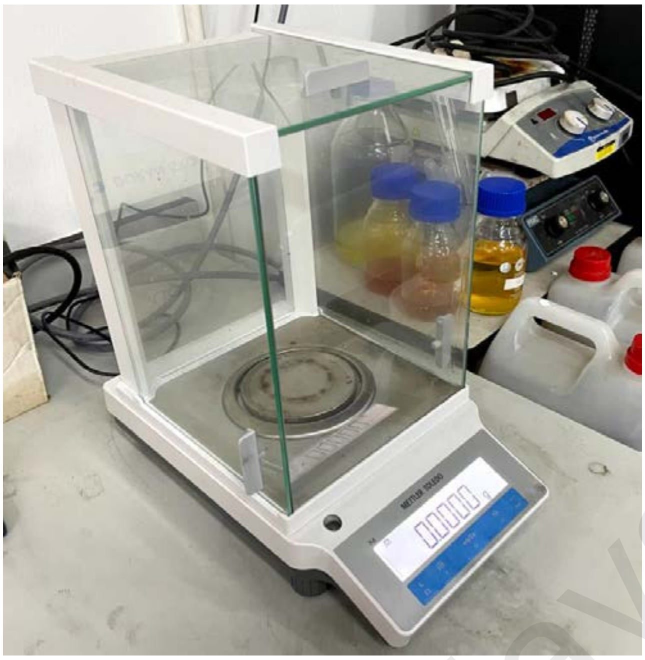


Figure 3.3: Electronic scale used to measure each of the weight of the component.

Upon completion of mixing, the sample is now transferred into a sealed sample container and labelled accordingly for the next process, as shown on Figure 3.4 below.

Figure 3.4: All 6 samples are prepared and sealed in a container to prevent containimation.

3.4 Measurement of Sample Physicochemical Properties

Each sample produced is tested using a viscometer (SVM 3000 Stabinger Viscometer) to obtain its kinematic viscosity, dynamic viscosity, viscosity index and density. Both of the kinematic viscosity and dynamic viscosity are obtained at 40 degree Celsius and 100 degree Celsius.

The viscometer used is compliant to measuring standard of ASTM D2270 with accuracy of ±0.35%, ±0.01% and 0.0001 g/cm^3 for viscosity, viscosity index and density, respectively.

Before each sample is added into the viscometer, acetone is used to clean the viscometer thoroughly to ensure no leftover residue from previous test. Acetone is feed into the inlet of viscometer until is visible at the outlet – this is to ensure the entire feeding line is cleared. Once the feeding line is cleaned, a small amount of sample is added before running the viscometer to obtain the results.

3.5 Summary of Properties Obtained from Physiochemical Analysis

A number of parameters are obtained through the physiochemical analysis using the viscometer is tabulated in Table 3.3 below.

Table 3.3: Properties of Physiochemical Analysis to be examined.

Properties	Temperature
Kinematic Viscosity (mm2/s)	40 °C
	100 °C
Dynamic Viscosity (MPa.s)	40 °C
	100 °C
Viscosity Index	-
Density (g/cm3)	15 °C

3.6 Engine Run Test on Spark Plug of a Two-Stroke Engine

The engine being used to mimic a marine outboard engine is a two-stroke engine from Mercury – the specification is as shown in Table 3.4 below. The two-stroke engine is attached on a 200 liters water drum half-filled with water to simulate a marine engine running. The setup of the experiment test is shown in Figure 3.5 below.

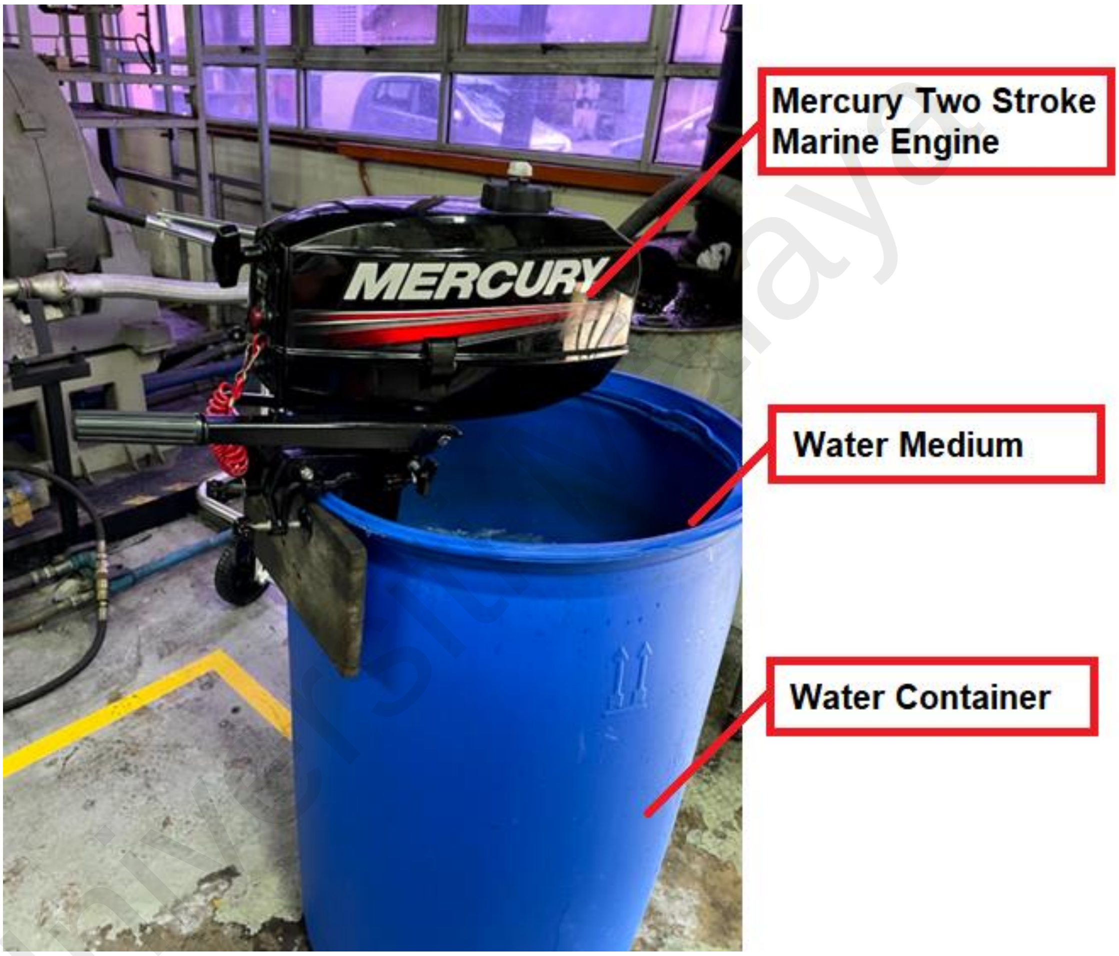


Figure 3.5: Setup of the experiment with the two-stroke marine engine.

For a 40:1 of fuel to lubricant ratio, measured using a measuring cylinder, 1 liter of fuel – RON 95 petrol, is mixed with one sample of the 2T Oil Mixture prior added into the two-stroke engine. A new spark plug is installed in the two-stroke engine and the two-stroke engine is crank-started and allowed to be run until all the fuel mixture is used up. The duration of engine run is expected to be approximately one hour for all the samples tested. The two-stroke engine is set at low speed and idling to prevent any external influence that would affect the result.

Once the two-stroke engine has stopped running, the water sample is collected and the spark plug is removed for observation and being recorded. The process is repeated again for the next sample until all the sample is completed.

For control experiment, the engine is run with the recommended commercial and non-bio-based lubricant once to allow us to compare the result.

Table 3.4: Specification of the two-stroke marine engine.

Model	Mercury ME 3.3 MH
Engine Type	2 Stroke / 1-Cylinder
Displacement	74.6cc
Fuel System	Carb
Lubrication System	Pre-mix
Recommended Lubricant	Quicksilver Premium 2-Stroke Outboard Oil
Exhaust System	Above Prop
Ignition System	CDI
Trim & Tilt	Manual
Gear Ration	2.15 : 1
Shaft Length	15 inch
Dry weight	13kg (with propeller)

CHAPTER 4: RESULT AND DISCUSSION

4.1 Physiochemical Properties of Bio-based Lubricant

The physiochemical properties being examined in this study include the kinematic viscosity, dynamic viscosity, viscosity index and its density. These properties are crucial to determine the behavior of the lubrication as its affect the internal friction between two contact surfaces in the two-stroke marine engine. As dynamic viscosity represent the resistance for fluid to flow, higher magnitude represent it has higher resistance to move at the direction of substance's motion. Similarly to dynamic viscosity, the kinematic viscosity measure the viscosity characteristic of the substance without the influence of external forces – solely only by gravity itself. Higher magnitude of kinematic viscosity represent higher internal resistance of the substances. Viscosity index in this study indicates the capability of the lubricant to operate at wide range of temperature while retaining its performance. Higher viscosity index represent it is more resistance towards changes when the temperature fluctuate from one point to another. Result of the physiochemical properties examined for the bio-based oil samples and reference sample is tabulated in Table 4.1 below.

Table 4.1: Physiochemical properties of bio-based oil and reference samples.

Base Oil Sample	Kinematic Viscosity (mm^2/s)		Dynamic Viscosity (MPa.s)		Viscosity Index	Density (g/cm^3)
	40 °C	100 °C	40 °C	100 °C		15 °C
Sample Baseline	72.197	10.399	61.705	8.493	129.5	0.855
Sample 1	57.163	9.122	48.616	7.324	139.3	0.870
Sample 2	50.995	8.800	43.430	7.154	152.1	0.868
Sample 3	47.114	8.545	40.163	6.956	160.4	0.869
Sample 4	56.624	9.507	48.306	7.724	151.6	0.870
Sample 5	54.722	9.454	46.761	7.719	156.9	0.870
Sample 6	55.246	9.476	47.314	7.727	155.6	0.874

Based on the result, among the bio-based oil samples, Sample 1 has the highest magnitude of kinematic viscosity and dynamic viscosity at 40 °C. Whereas at operating temperature of 100 °C, Sample 4 and Sample 6 have the highest magnitude for kinematic viscosity and dynamic viscosity, respectively. This is likely due to the presence of higher amount of the Group II mineral oil in the sample as Sample 1 is made up of 70% of it in the base oil. We observed the similar readings for TMP samples (Sample 4 – Sample 6) where Sample 4 has the highest viscosity at 40 °C as they are also made up of 70% of Group II mineral oil in the base oil. However, comparing with the baseline sample lubricant blend recommended by the two stroke marine engine manufacturer, Sample 4 is at average of 21% lesser than the baseline sample value.

At higher engine operating temperature or at 100 °C in this case, samples from TMP have higher viscosity rating on both kinematic viscosity and dynamic viscosity. This is due to the molecular structure of TMP whereby the higher the chain length and branching, the higher the viscosity rating (Hatzikiriakos & Science, 2000).

As for viscosity index (VI) from Table 4.1, Sample 3 has the highest magnitude compared to all of the samples – including the reference baseline sample. VI rating is crucial aspect to select an ideal lubricants for engine – especially for application whereby the engine will run in various external temperature environment and varies loading – be it in high load or low load. With a high VI, it indicates that the lubricant will resist to be thicken at low temperature and thinning at high temperature. Retaining its viscosity at low temperature or at starting of engine allow rapid start-up of engine without required to be pre-heated, whereas at high temperature or at high load and RPM allows the lubricant to provides full lubrication between the surfaces without thinning of lubricant, thus resulting in less stress to the engine (Zulkifli et al., 2013).

The above indicates that Sample 3 is the most ideal choice on the VI to perform the best at the temperature change occurred in the engine while retaining its lubricating properties. Hence, by addition of bio-based oil in the blend of 50% NPG ester lubricant, the VI has improved by 23.86% comparing with the baseline sample lubricant blend recommended by the two stroke marine engine manufacturer.

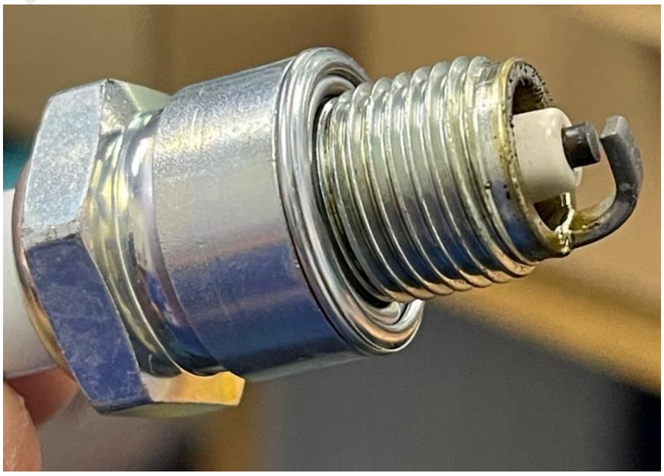
Density of the bio-based lubricants varies no more than 3% from the baseline sample – hence it does not play an important role in the selection of the optimum lubricants for the two-stroke marine engine.

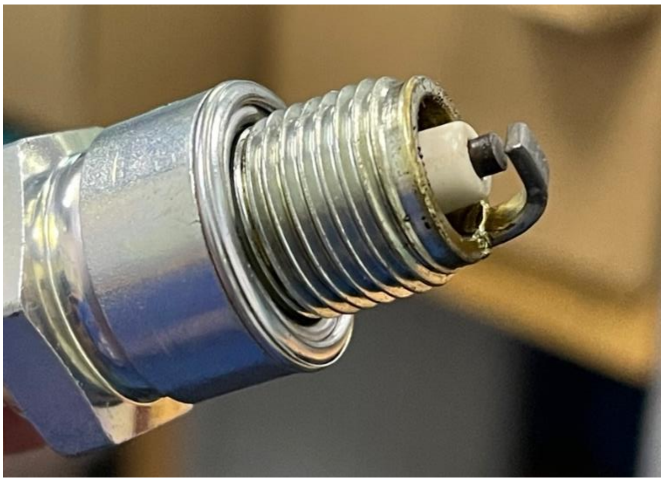
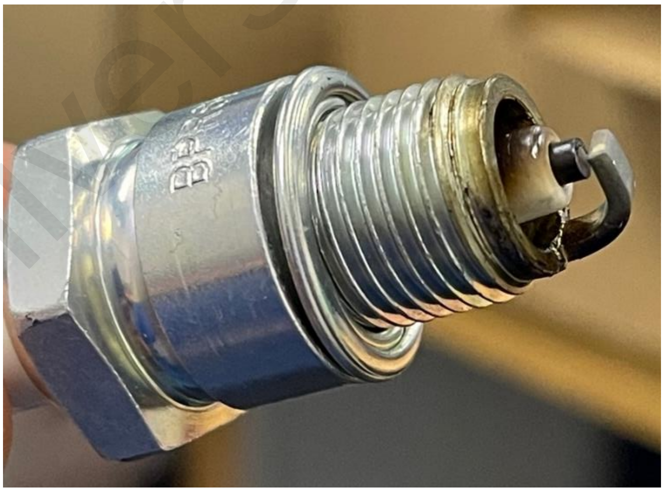
4.2 Carbon Deposition Observation on Marine Engine Test Run

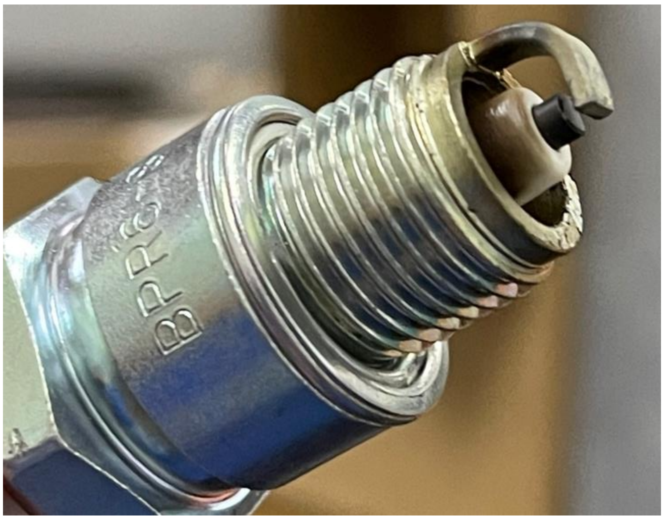
All of the based oil samples are tested in the two-stroke marine engine with a new spark plug. The engine is filled with equal amount of fuel mixture for each sample and allowed to be run until the fuel runs out. The range of engine running duration range is at average of 2 hours at approximately 80% of maximum throttle.

The spark plug is removed and examine by observation to determine the condition of the spark plug and the observation is recorded as per Table 4.2 below. A new spark plug is installed prior to running the next sample.

Table 4.2: Spark plug observation after performing marine engine test run.

Samples	Observation	Verdict
Sample - Baseline		Moisture: Dry Carbon Deposits: Visible
Sample 1		Moisture: Dry Carbon Deposits: None
Sample 2		Moisture: Dry Carbon Deposits: None

Sample 3		Moisture: Dry Carbon Deposits: None
Sample 4		Moisture: Dry Carbon Deposits: None
Sample 5		Moisture: Dry Carbon Deposits: Visible

Sample 6		Moisture: Dry Carbon Deposits: Visible

From the observation tabulated in Table 4.2, it is clear that bio-based oil containing PNAF-NPG produces dry and cleaner deposit on the spark plug and combustion chamber. This result indicate that combustion is complete and minimal by-product will be introduced into the marine environment during the engine operating using this mixture. Similar results are observed whether the concentration of PNAF-NPG is at smaller or larger range. However, the selection of the most optimal range has to be considered with the result from physiochemical properties.

Whereas for bio-based oil containing TMP, at larger concentration (>30%), it produces significant amount of carbon deposition around the spark plug and this indicatively tells that the combustion of this mixture is harder and incomplete. This would introduce large amount of by-product into the marine environment when operating in long term. The result from baseline sample has the similar observation on the spark plug when using TMP bio-based oil. The combustion for both bio-based oil are largely affected by the molecular structure of the substances. NPG has a much simpler molecular structures compared to TMP, hence the combustion will tend to be easier and much more complete on a NPG bio-based oil. Similar result as above is observed in previous study on TMP ester bio-based lubricant (Zulfattah et al., 2019).

4.3 Carbon Deposition Observation on Grass-Cutter Engine Test

A similar separate experiment and test on grass-cutter engine was performed and the results from the observation is obtained to perform a comparative study using the similar 2T bio-based oil mixtures with a marine outboard engine. The setup of this engine test was done on a separate study, hence it is not shown in the Chapter 3 – Methodology. However the results are obtained below to serve as a comparison with the marine engine. The observation of the spark plug upon test where recorded and obtained as shown in Table 4.3 below.

Table 4.3: Spark plug observation after performing grass-cutter engine test run.

Samples	Observation	Verdict
Sample - REF		Moisture: Dry Carbon Deposits: Heavy

Sample 1		Moisture: Dry Carbon Deposits: None
Sample 2		Moisture: Dry Carbon Deposits: Minimal
Sample 3		Moisture: Wet Carbon Deposits: Moderate

Sample 4		Moisture: Wet Carbon Deposits: Moderate
Sample 5		Moisture: Wet Carbon Deposits: Moderate
Sample 6		Moisture: Wet Carbon Deposits: Heavy

From the results tabulated in Table 4.3, carbon deposition occurred in most of the samples, except for Sample 1. This indicates that improper heat range or incomplete combustion occurred during the operation of the grass-cutter engine.

The condition on the spark plug is also found to have certain level of moisture or 'greasiness' upon combustion – this is likely due to the incomplete burn of the fuel and lubricant mixture. This condition is observed largely from Sample 4 to Sample 6 where TMP bio-based oil is used at the lubricant. This result indicates that the complex molecular structure of TMP will required higher heat energy and temperature for it to complete its combustion process. Incomplete burn during combustion and hence indicatively it has weak ignition in the combustion chamber causes large amount of carbon deposition on the spark plug. As for PFAD-NPG ester, the similar condition is observed at higher concentration of the bio-based oil.

However, this is not observed during the engine test run using a marine engine as the marine engine operate at much higher revolution and higher temperature – this would assist the combustion of the TMP bio-based oil during the operation.

4.4 Water Sample Observation

Water sample collected from the water medium where the engine propeller is submerged after each of the engine test run is observed and examine manually by hand to interpret its condition. All of the water sample collected from Sample 1 to Sample 6, including the baseline lubricant's sample turns out to be murky and cloudy with slight oily condition to touch. This condition is expected and it is due to the fuel and lubricant mixture precipitate that has been released from the two stroke engine during combustion process.

The water sample also emits slight exhaust fume odor due to the dissolved exhaust gas being "filtered" through the water before releasing into the air. Figure 4.1 below shows one of the water sample collected after the engine test run process. For further analysis, the water sample will be sent for in-depth analysis given the chance in the future with adequate access to proper equipment and funding. Water sample analysis is not performed in this research and will be considered as future work.

Figure 4.1: Water sample collected from the water medium after complete one of the engine run test.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

The physicochemical properties of all the samples with various compositions are obtained using a viscometer. From the samples - including the baseline sample, Sample 3 with 50% PFAD-NPG and 50% mineral oil mixture, gives the most optimum composition as its physicochemical properties exhibited satisfactory results with improvement of 28.36% in terms of Viscosity Index, compared to the baseline sample. Whereas for its kinematic and dynamic viscosity, Sample 3 delivers an improvement of average 18% comparing to the baseline sample - followed by Sample 2 with average of 15% improvement. Low viscosity value for both kinematic and dynamic are crucial to ensure least resistance is subjected on the engine piston during operation while maintaining the lubricating film layer to prevent engine damage. This would also result in lesser stress on the engine thus prolong the lifecycle of the two-stroke marine engine. Thus, in order to improve the performance of engine oil, retain 50% of the lubricant mixture with NPG ester bio-based oil will result in the most acceptable performance.

Whereas for carbon deposition on spark plug upon engine test run, when the composition of bio-based oil with mineral oil is correctly quantified, it will improve the condition of spark plug in terms of carbon deposition. NPG ester bio-based lubricant (Sample 1 to Sample 3) produce the cleanest result with minimal to none carbon deposition - compared to the baseline sample where slight and visible carbon deposition is observed. While TMP ester bio-based oil (Sample 4 to Sample 6) is another alternative bio-based oil, higher ratio of TMP ester to Group II mineral oil would result in negative effect whereby large amount of carbon deposition is found on the spark plug. To avoid this, based on the engine test, maintaining the TMP ester level less than 30% of the base oil mixture would result in positive result.

While running the samples in a marine engine would means the engine oil is tested at higher RPM, the samples are tested in grass cutter engine to examine its behavior at low revolution settings. From the engine test result, PFAD-NPG ester perform the best compared to TMP ester – where significant carbon deposition and unburnt fuel and oil mixture are found at TMP ester samples. This indicates that the complex microstructure of TMP required higher heat energy to undergo combustion. It can be deduced that the usage of PFAD-NPG ester as 2T oil base component is acceptable for wide range of application. Thus, from the conclusion above, all of the objectives in this study have been achieved and quantified.

5.1 Future Work

From the above research, a number of future study can be done based on the current setup to further explore the benefits of bio-based oil, mainly using NPG and TMP ester. The future would also be useful to strengthen the result obtained from this research. A number of future can be done, mainly they are:

- Varies the ratio of fuel to oil mixture in the engine to explore other possibility of fuel to oil ratio in marine engine.
- Perform water sample analysis of the water medium obtained after engine run test to study the components and pollutants in the water medium.
- Different composition between bio-based oil and mineral oil.
- Different amount of solvent and additive package and using more base oil in the mixture to examine the behavior of the lubricant and discover its capability.

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