Chemical And Viscosity Profile Of Bio-Based High Performance Engine Oil For IC Engine

Harizal Hamid [1], *, Zuraida Khairudin [3] Muhidin Arifin [2], M. Hakimi[1], Nurazlina.I[1]

[1] Department of Science and Biotechnology, Universiti Selangor, 45600 Selangor, Malaysia
[2] Department of Engineering, Universiti Selangor, 45600 Selangor, Malaysia
[3]Statistical and Decision Science Studies, UiTM Shah Alam,40450 Selangor,Malaysia.

***Correspondence:** harizal@unisel.edu.my

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Abstract- The use of lubricants that are based on vegetable oils is increasing rapidly due to their biodegradability, low ecotoxicity and excellent tribological properties. Bio based lubricants have lower coefficient of friction, improved wear characteristics, a higher viscosity index, and lower volatility and flashpoints than mineral based oils, Properties of the Bio-based based lubricants could be enhanced by adding additives and diluting with other synthetic oils. However, in many cases additives and synthetic fluids are not sufficient. In such occasions chemical modification is a better alternative. GC/MS analysis of bio based, indicated that the major hydrocarbon present in fresh synthetic oil was tetratriacontane ($C_{34}H_{70}$) and docosane ($C_{22}H_{46}$) is characterized as hydrocarbon lipid molecule. Bio-based formulated engine oil show a stable and significant value of kinematic viscosity compared to the commercial semi synthetic oil. At 60^0C the viscosity value for Bio-based formulated oil score a higher value at 12.8mm^2/s comparing to the commercial semi synthetic sample at 11.4mm^2/s

Index Terms- Engine oil,Bio-Based lubricant,chemical analysis profile,kinematic viscosity

I. Introduction

The moving forward automotive industries are demanding a continuous development of new technology and new approach of current technologies available which lead to the creation of new materials and applications in automotive technologies and application that is more themed to improved performance, cost-effective, environmentally-friendly, resource and technology acquisition and approaches that meet customer requirements. [1]

In an engine, oil serves multiple purposes. It greatly reduces friction between moving parts, and therefore reduces wear and tear. Oil moves heat from very warm parts to cooler areas in the engine, and stops corrosion, which occurs when metal parts are exposed to oxygen. Oil also cleans dirty engine parts, thanks to added detergents that keep the engine clean and prevent oil sludge. [2] They feature resistance to high temperature oxidation, good film strength, and stable viscosity and rarely cause harmful engine deposits. Motor oils are a complex blend of many ingredients, but they're made up of two primary elements -- base oil and additives. With conventional oil, crude oil is refined extensively until suitable base oil is achieved. Less refined portions of the crude are much thicker and used for different applications, such as roofing tar or road asphalt.[3].

Production of the Bio-based based engine oil lubricants are formulated by adding additives and diluting with other compound polymer. In such occasions chemical modification is a main approach in order to achieve the desired properties for the fluid to working efficiently. [4] Thermal polymerization and transesterification are the main process to enhance the chemical capabilities of bio based oil (olive oil and oil palm oil) to fit the requirement in internal combustion engine. Thermal polymerization increases the viscosity of the base fluid by anaerobically heating it and transesterification replaces glycerol with other alcohols to alter low temperature properties and viscosities.

Bio-based materials currently being classified as a major element in playing a part as an alternative to chemical based products due to the environmental concern as a pollutions factor are mainly the main concern in nowadays. Researchers and scientist tend to seek alternatives since our industries are mainly dependence on petroleum and chemical based product that having a several after effect problem such as the unstable price of the material and high-decompose resistance. The interest in bio-based materials has been accelerated as a result of the increasing prices of crude oil. Chemical modification of vegetable oil is necessary in order to compete with petroleum products.

II. Literature Review

The use of lubricants that are based on vegetable oils is increasing rapidly due to their biodegradability, low ecotoxicity and excellent tribological properties. Bio based lubricants have lower coefficient of friction, improved wear characteristics, a higher viscosity index, and lower volatility and flashpoints than mineral based oils. Polymerized vegetable oils have found their way into many industrial applications such as inks, polymers, and hydraulic fluids. The initial objective of this research is to formulate a bio-based engine lubricant from thermally polymerized vegetable oils. [5]

Bio-based oil is biodegradable and nontoxic which is a benefit over mineral based oils [18]. Bio-based oil has low volatility because of their high molecular weights. Moreover, they have good lubricity due to their ester groups. Also vegetable oils have higher viscosity index (VI) which indicates that they are less sensitive to viscosity change with temperature. However vegetable oils mainly suffer from poor oxidative stability and low-temperature solidification. These properties could be improved by additives and chemical modifications [3]. Chemical structure of vegetable oil makes it very delicate to oxidation. Since vegetable contain mostly oleic, linoleic and linolenic fat fatty acids they all have carbon double bonds which oils decrease the oxidation stability. Allylic methylene groups are more stable than double allylic methylene groups thus oleic acid is much more stable than linoleic and linolenic acids. On the other hand carbon double bonds increase the low temperature properties [6].

Properties of the Bio-based based lubricants could be enhanced by adding additives and diluting with other synthetic oils. However, in many cases additives and synthetic fluids are not sufficient. In such occasions chemical modification is a better alternative [7] . Many chemical modifications have been introduced. Thermal polymerization and transesterification are the main process to enhance the chemical capabilities of bio oil to fit the requirement in IC engine. Thermal polymerization increases the viscosity of the base fluid by anaerobically heating it and transesterification replaces glycerol with other alcohols to alter low temperature properties and viscosities. Furthermore, the use of lubricants that are based on vegetable oils is increasing rapidly due to their biodegradability, low ecotoxicity and excellent tribological properties. Bio-based lubricants have lower coefficient of friction, improved wear characteristics, a higher viscosity index, and lower volatility and flashpoints than mineral based oils.

III. Experimental Method

Production of the Bio-based based engine oil lubricants are formulated by adding additives and diluting with other compound polymer. In such occasions chemical modification is a main approach in order to achieve the desired properties for the fluid to working efficiently. Thermal polymerization and transesterification are the main process to enhance the chemical capabilities of bio based oil (olive oil and oil palm oil) to fit the requirement in internal combustion engine. Thermal polymerization increases the viscosity of the base fluid by anaerobically heating it and transesterification replaces glycerol with other alcohols to alter low temperature properties and viscosities.

Based Oil	**Function**	**(%)**
Oil palm oil	Base	35%
Olive Oil	Base	15%
Additive	**Function**	**(%)**
Molybdenum disulfide (Mos2)	Friction modifier	5%
Boric acid; orthoboric acid (B2O3 3H2O, H3BO3	Friction modifier	7.5%
High purity Nano TiO_2	Antiwear agents	2.8%
Olifien Co-polymer	Viscosity Index Improver	3.5%
Triazolas	Anti-rust/corrotion	1.5%
Calcium Sulfonates	Detergent	13%
zinc dialkyldithio phosphate	Anti-ware agent	4.5%
Compound Polymer	Performance Addivite	12%

Table 1. Basic Formulations for Bio-Based Engine Oil

IV. Comparison Method

Two different commercially available four-stroke engine oil were used as sample references. The selected oil was synthetic type, where the rest of the sample was selected from semi-synthetic category. The existing engine oil were used as references in comparing the physical and chemical properties of the formulated Bio-Based engine oil.

No	Oil Type	Manufacturer	Viscosity class
1.	Commercial Fully Synthetic oil	Local	10W-40
2.	Commercial Semi Synthetic Oil	Local	10W-40
3.	Bio-based formulated oil with 50% based oil	- Nil	-Nil

Table 2: Type of Engine Oil as references

V. Physical and Chemical Analysis

The lubricants were characterized from a physical-chemical point of view through standard analytical techniques. Gas chromatography were used to perform analytical measurement of the initial profile of the oil subjected to the polymerization of the bio-based crude oil. The presence of additives elements present in engine oils was determined using inductively X-Ray Fluorescence (XRF), Model Minipal infinite series, USA according to the ASTM standard (D5185). Kinematic viscosities were measured according to the ASTM standard (D445) and viscosity index according to (D2270). Water content was determined according to (D1744). Finally, total acid number (TAN) and total base number (TBN) was measured according to (D4739) ASTM and (D664) respectively. The reference norms can be found on the ASTM's website.

VI. Experimental Method

a. Gas Chromatography Analysis (Polymerization Profile)

A polymerization of Bio-based oil is a liquid composed of monomer, oligomer, initiator and additives. It will create layers of film in a period of time under the influence of temperature. In this report, a polymerization of Bio-based oil was analyzed by electron ionization (EI) and field ionization (FI).

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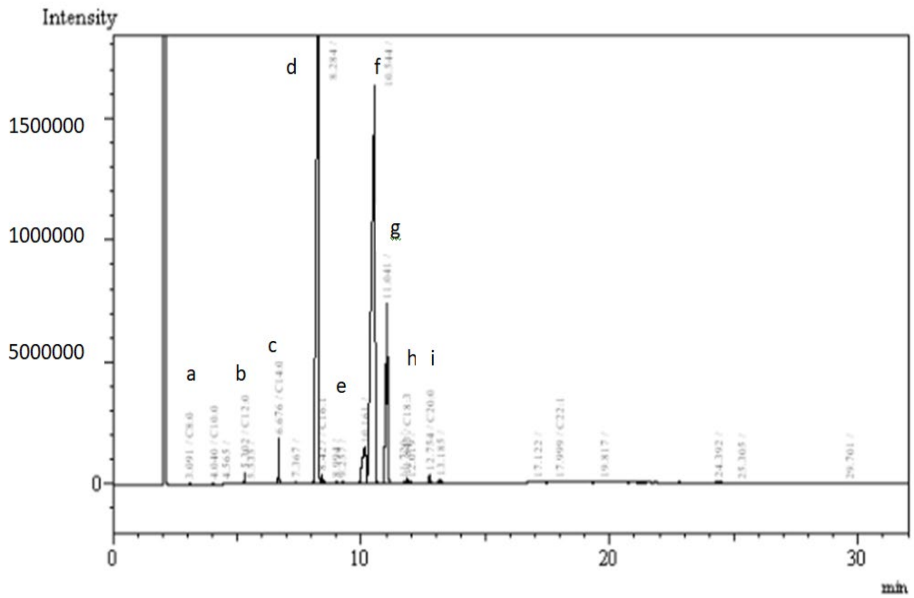

Figure 1: Polymerization Profile for Bio-Based Engine Oil

Compound	Retention Time (min)	Area %
a..Tetratriacontane	20.66	13.08
b..Docosane	16.08	9.62
c.Tetracosane	20.81	6.53
d..Dotriacontane	6.90	0.71
e.Tetrapentacontane	25.41	5.45
f. Hexacontane	74.59	5.11
g.Hexadecane	61.90	0.55
h,Pentadecane	11.446	.66
i.Hexadecane	12.926	0.65

Table 3: List of Active Compound In Formulated Bio-Based Engine Oil Characterized by GC/Ms

GC/MS analysis of bio based, synthetic and semi-synthetic oil samples was performed to identify the different species originally present comparing to each other. As the oil contains complex mixture of different organic compounds, the area% contribution of the various hydrocarbons is shown in **Table 1** for different conditions. It is clear that the major hydrocarbon present in fresh synthetic oil was tetratriacontane ($C_{34}H_{70}$), while docosane ($C_{22}H_{46}$) is characterized as hydrocarbon lipid molecule. Docosane is a very hydrophobic molecule, practically insoluble (in water), playing a role in anti-corrosion in engine working principles.

Theses compound categorized in alkanes that have a higher viscosity contributed to the most important components of lubricating oil. In addition of anti-corrosive agents, as the main properties of theses alkanes are hydrophobic nature means that water cannot reach the metal surface in internal combustion engine.

b. X-RF Analysis

Additives are substances that improve the anti-friction, chemical and physical properties of base oils, thus enhancing the lubricating performance of the oil and extending the equipment life. The combination of different additives and their quantities are determined by the type of lubricant (engine or gear oils, hydraulic oils, cutting fluids, compressor oils, etc.), the specific operating conditions (temperatures, loads, contamination levels, etc.) and the need to extend the intervals between oil changes. From the XRF elemental analysis the main elements in the formulated Bio-based engine oil : Zink(Zn), Rhenium(Re), (Calsium)Ca, Manganese(Mn), and Sc Zink(Zn), mainly from zinc dialkyldithio phosphate play part in lubricating as an antioxidant and an anti-wear additive

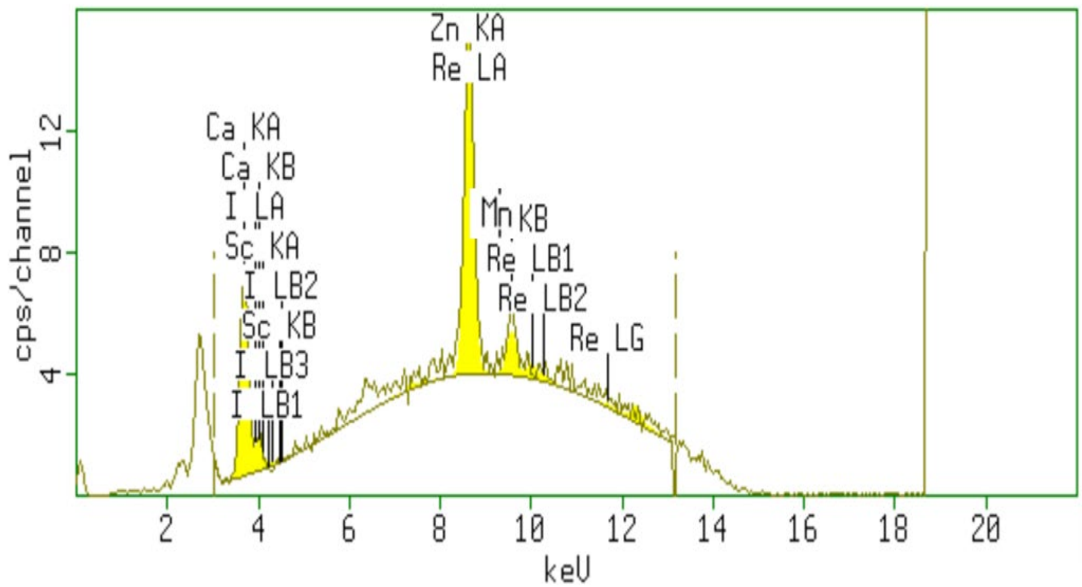

Figure 2: XRF Profile For Bio-Based Engine O

VII. Kinematic Viscosity

In the experimental procedure, a volume of (300 ml) of formulated oil was put into the apparatus cuvette by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. The dynamic viscosity, **η**, can be obtained by multiplying the kinematic viscosity, **ν**, by the density, **ρ**, of the liquid.

Kinematic Viscosity is the ratio of absolute or dynamic viscosity to density – a quantity in which no force is involved. Kinematic viscosity can be obtained by dividing the absolute viscosity of a fluid with it's mass density,

$$\nu = \eta / \rho,$$

where

ν = kinematic viscosity
η = absolute or dynamic viscosity
ρ = density

No	Oil Type	v at 40^0	v at 60^0	v at 80^0	v at 100^0
1.	Commercial Fully Synthetic oil	22.4	13.2	9.4	6.72
2.	Commercial Semi Synthetic	22.6	11.4	8.7	5.45
3.	Bio-based formulated oil	25.4	12.8	9.5	6.12

Table 4: The values of kinematic viscosities (cSt) of samples at different temperatures.

As mentioned before the viscosity of lubricating oil is a play a crucial part in the lubricating oil behavior in IC engine. The kinematic viscosity was measured at different temperature ranging from 40^0 to 100^0 C for all samples to determine the kinematic viscosity value. The results are shown in **Table 4** and **Fig. 3**, where the viscosity decreases with raising the temperature; this is attributed to the thickening effect. This effect is much greater at 100 ^{0}C than at 40 ^{0}C.[8]

From the data we can conclude that for the overall samples the viscosity drops intensely from 40 to 100°C. These can be explained to the adhesion forces between inter-molecular and inter-particle that constantly loss the rate of bonding between them as the temperature increased. The decreasing of Brownian diffusion at particular temperatures also one of factor contributed to lower viscosity value.

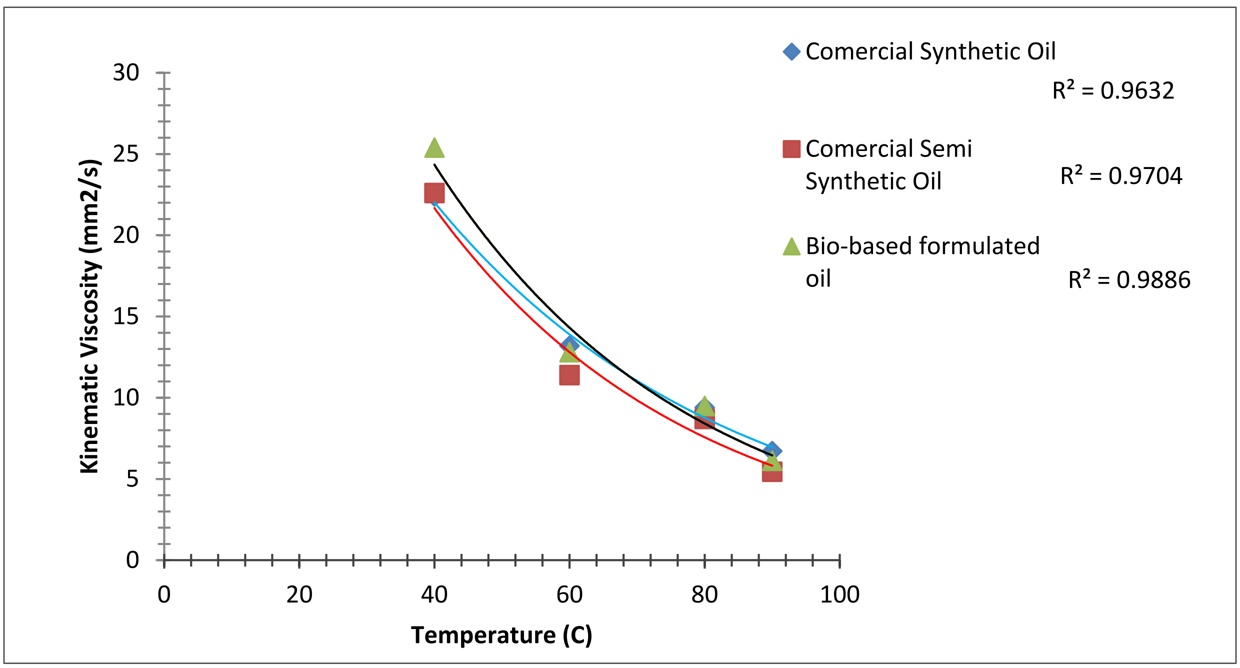

Figure 3 : Kinematic Viscosity Of Selected Oil Type At varies Temperature

Bio-based formulated engine oil show a stable and significant value of kinematic viscosity compared to the commercial synthetic oil. At 60^0C the viscosity value for Bio-based formulated oil score a higher value at 12.8mm^2/s comparing to the commercial semi synthetic sample at 11.4mm^2/s

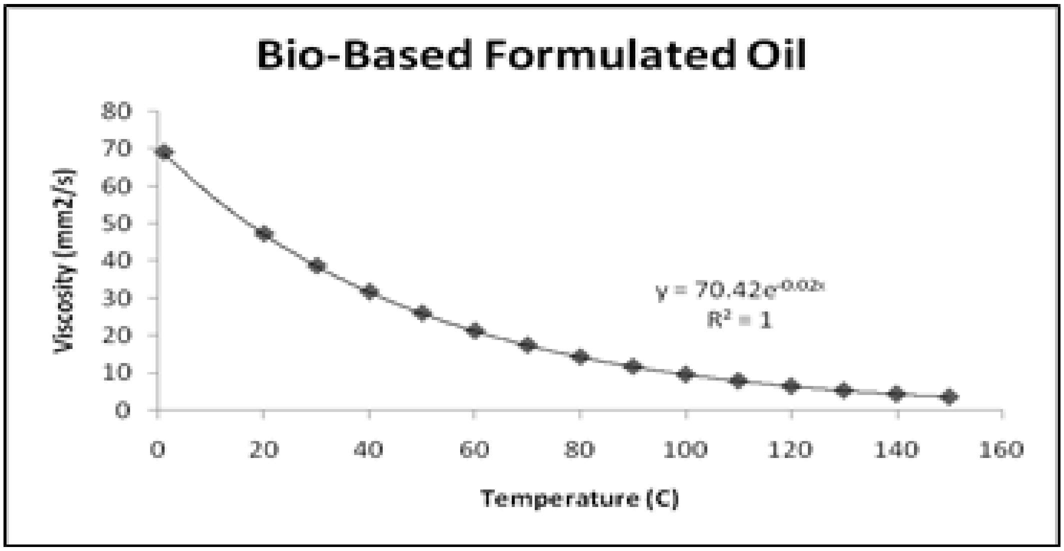

Figure 4 : Kinematic Viscosity Profile Of Bio Based Formulated Oil

The experimental data for Bio-based formulated oil kinematic viscosity is used to make a profile of the formulated engine oil at the predicted temperature as shown in **Figure 4**. These profile data are important as the profile reference for the formulated engine oil at Field testing and engine test run. The profile of the kinematic viscosity derived from the exponential equation from the experimental data $y=70.42e^{-0.02x}$, as x represent the temperature.

Determination of viscosity index of oil is calculated from its viscosities at 40 and 100°C. The procedure for the calculation is given in ASTM Method D 2270-74 for Calculating Viscosity Index from Kinematic Viscosity at 40 and 100C. **Table 5** lists the basic viscosity values of the reference series used in the calculation. The accuracy of the calculated viscosity index Fobtained by the use of Method D 2270.[9]

No	Oil Type	v at 40^0	v at 100^0	v Index
a	Commercial Fully synthetic oil	22.4	6.72	290
b.	Commercial Semi Synthetic Oil	22.6	5.45	193
c.	Bio-based formulated oil with 50% based oil	25.4	6.12	204

Table 5: Viscosity Index for The (a) Commercial Fully Synthetic Oil, (b) Commercial Semi Synthetic Oil, (c) Bio-based formulated oil.

A higher viscosity index is desired as the maintenance of forming the lubricating film, on the other hand the index should be low enough to make sure that the lubricant oil can flowing easily to every specific part of IC engine. The viscosity index is a measure of how much the oil's viscosity changes as temperature changes. A higher viscosity index indicates the viscosity changes less with temperature than a lower viscosity index. A higher viscosity index indicated that the much smaller viscosity change with increasing in temperature.[10]

VIII. Conclusion

The overall chemical analysis of the Bio-Based formulated lubricant indicated a promising characteristic as high performance lubricant in IC engine. The value of the kinematic viscosity also seems higher than ordinary semi-synthetic engine oil as the formulation Bio-based oil score a higher value at 12.8mm^2/s. A viscosity index value at 204 as the value as the ration of kinematic viscosity at 40^{0}c and 100^{0}c

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AUTHORS

First Author – Harizal Bin Hamid, Master in Physics, Univerisiti Selangor, harizal@unisel.edu.my .
Second Author – Zuraida Bte Khairudin, MSC in Statistics, UiTM, zuraida_k@tmsk.uitm.edu.my .
Third Author – Accosiate Professor Ir Muhidin Bin Ariffin , Phd in Mech , Univerisiti Selangor, irmuhidin@unisel.edu.my

Correspondence Author – Harizal Bin Hamid, Master in Physics, Univerisiti Selangor, harizal@unisel.edu.my , harizalhamid@gmail.com, phone number+-601287958452