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POTENTIAL OF PALM OLEIN AS GREEN LUBRICANT SOURCE: LUBRICATION ANALYSIS AND CHEMICAL CHARACTERISATION

(Potensi Minyak Sawit Olein Sebagai Sumber Lubrikan Hijau: Analisis Pelinciran dan Pencirian Kimia)

Darfizzi Derawi* and Jumat Salimon

School of Chemical Sciences and Food Technology,
Faculty of Science and Technology,
Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

**Corresponding author: darfizzi@ukm.edu.my*

Abstract

Palm olein (PO_o) is widely used as edible oil in tropical countries. The lubrication properties and chemical compositions of PO_o being considered to be used as renewable raw material for biolubricant synthesis. PO_o is suitable to be used directly as biolubricant for medium temperature industrial applications. Palm olein has good viscosity index, oxidative stability, flash and fire point as a lubricant source. PO_o contains unsaturated triacylglycerols (TAG): Palmitin-Olein-Olein, POO (33.3 %), Palmitin-Olein-Palmitin, POP (29.6 %), which are very important to produce good lubricant properties. This unsaturated bond is preferable in chemical modification to produce biolubricant. The chemical compositions of PO_o were tested by using high performance liquid chromatography (HPLC) and gas chromatography (GC) techniques.

Keywords: Palm olein, Renewable Source, Lubrication Analysis, Biolubricant

Abstrak

Minyak sawit olein (PO_o) digunakan secara meluas sebagai minyak masak bagi negara-negara beriklim tropika. Sifat-sifat pelinciran dan komposisi kimia PO_o dinilai untuk digunakan sebagai bahan mentah dalam sintesis biolubrikan. PO_o sesuai digunakan secara terus sebagai biolubrikan untuk aplikasi industri bersuhu sederhana. Minyak sawit olein adalah baik sebagai sumber lubrikan berdasarkan indeks kelikatan, kestabilan oksidatif, takat kilat dan api. PO_o mengandungi triasilgliserida tak tepu (TAG): POO (33.3 %), POP (29.6 %) iaitu sangat pnting untuk menghasilkan sifat-sifat lubrikan yang baik. Ikatan tak tepu diperlukan dalam modifikasi kimia untuk menghasilkan biolubrikan. Komposisi kimia PO_o diuji menggunakan teknik kromatografi cecair berprestasi tinggi (HPLC) dan kromatografi gas (GC).

Kata kunci: Minyak Sawit Olein, Sumber Boleh Diperbaharui, Analisisi Pelinciran, Biolubrikan

Introduction

Lubrication industry plays an important role in the national economic sector. This leads to the improvement of research and development in lubrication industries particularly on the synthesis works by using different raw materials. Conventionally, lubrication industries use petroleum based sources as the raw materials. Recently, researchers all over the world talked about the new approaches in chemical synthesis techniques to produce industrial products such as polymers, fuels and lubricants [1]. As a result, some of the environmental friendly sources that can initiate green technology in chemical synthesis were found out. Commonly, these sources had been used traditionally as herbs or food usage for a long time. Because of the lack of scientific researches, the potential of these crops as natural friendly sources on developing the industrial products are not being discovered.

Palm oil is from the fleshy endosperm of oil palm with its scientific name *Elaies guineensis* [2]. Palm oil undergoes some refinery stages such as fractionation distillation, refining, bleaching and deodorization to produce refined, bleached and deodorized palm oil (RBDPO). A single fractionation converts palm oil to palm olein by 75-80 % yield [3]. Palm olein (PO_o) is the most valuable liquid fraction of palm oil (the largest renewable resource in Malaysia). It is used for frying food and salad oils [2].

It mainly consists of mono-unsaturated triacylglycerol (TAG), palmitin-olein-palmitin (POP) (42.8 %) and di-unsaturated TAG, palmitin-olein-olein (POO) (35.7 %). The iodine value of PO_o is about 51.0 – 61.0 [4]. PO_o consists of oleic acid (42.7-43.9 %) and palmitic acid (39.5-40.8 %) [5]. Oleic acid is a mono-unsaturated fatty acid while palmitic acid is a saturated fatty acid attached to the TAG of PO_o. Oleic acid is needed to improve the pour point and cloud point value of PO_o. While, the palmitic acid is needed to improve the oxidative and thermal stability. Thus, the combination of mono-unsaturated and saturated properties of PO_o makes it preferable as raw materials in biolubricant production. In this paper, we report that the physico-chemical properties and chemical compositions of PO_o have promising potential to be developed as raw materials in biolubricant synthesis.

Materials and Methods

Raw materials

Palm Olein (Seri Murni brand, FFM Marketing Sdn. Bhd.) was purchased directly from the market.

Chemical composition tests

Gas chromatography analysis was studied via GC instrument, 17A Shimadzu model. The capillary column used is non-polar stationery phase (BPX70) with Helium as mobile gas. The initial temperature is 120 ^oC and final temperature is 250 ^oC with temperature rate 3 ^oC per minute. High Performance Liquid Chromatography (HPLC) analysis was performed by HPLC auto sampler instrument, Dionex Ultimate 3000 model with non-polar column (C18, 150 mm x 4.8 mm x 3 µm). The mobile phase used is a mixture of aceton : acetonitrile (60:40 v/v) [6].

Chemical characterization tests

The iodine value of PO_o sample was determined by Wijs method (British standard BS 684: Section 2.13:1976) [6]. It can be defined as a measure of the unsaturation of fatty acids and is expressed in terms of the number of centigrams of iodine absorbed per gram of sample (% iodine absorbed). The acidity of PO_o was determined by AOCS 5a-40 (1989) [6]. The acid value is the number of milligrams of potassium hydroxide required to neutralize the free fatty acids in 1 g of sample. The cloud point is the temperature at which, under certain test conditions (A.O.C.S. Cc 6-25), a cloud is induced in the sample caused by the first stage of crystallization [6]. The moisture content of PO_o tested by Karl Fischer method (A.O.C.S. Tb 2-64) [7]. This method is to determine the actual water content of oil by titration with Fischer reagent which reacts quantitatively with water. The saponification value (British standards BS 684 2.6:1977) [6] done to calculate the milligrams of potassium hydroxide (KOH) required to saponify 1 g of fat under the conditions specified. It is a measure of the average molecular weight of all the fatty acids present. 10 g of PO_o was used to test the unsaponifiable matter (A.O.C.S. Ca 6a-40) [6]. This method is to test the unsaponifiable matter includes those substances frequently found dissolved in oils which cannot be saponified by the caustic alkalies, but are soluble in the ordinary fat solvents which include higher aliphatic alcohols, sterols, pigments, and hydrocarbons.

Lubrication analysis

Oxidative stability of PO_o was tested by using Pressurized Differential Scanning Calorimeter (PDSC), Mettler Toledo DSC 822 model with StarE software [8]. A 10 ^oC min^{-1} heating rate (25 ^oC to 300 ^oC) was used for the test. The oxidation onset (OT, ^oC) and signal maximum temperatures (SMT, ^oC) were calculated from a plot of heat flow (W/g) versus temperature. Pour point can be defined as the lowest temperature, expressed as a multiple of 3 ^oC at which the oil is observed to flow when cooled and examined under prescribed conditions (ASTM D 97-66) [9]. The fire and flash point test as according to the ASTM D 92-78 [7]. The test cup was filled to a specified level with the sample. The temperature of the sample was increased rapidly at first and then at a slow constant rate as the flash point approaching. At specified intervals a small test flame was passed across the cup. The lowest temperature at which application of the test flame causes vapours above the surface of the liquid to ignite is taken as the flash point. In order to determine the fire point, the test was continued until the application of the test flame causes the oil to ignite and burn for at least 5 seconds. The kinematic viscosity of PO_o was tested by using Anton Paar rheometer

(Physica MCR 301 model) according to ASTM D 445-79 [7]. The viscosity index (ASTM D2270) was calculated by using the kinematic viscosity at 40 ^{o}C and 100 ^{o}C [10].

Determination of ISO Lubricant Grade

The classification of ISO lubricant grade according to the American Society of Lubrication Engineers (ASLE) and British Standards Institution (BSI) [11].

Results and Discussion

Chemical composition

Based on the GC analysis done, there was three major FFAs of PO_o (Table 1). These FFAs are oleic acid (47.7 %) followed by palmitic acid (36.3 %) and linoleic acid (10.4 %). The others are lauric acid (0.2 %), myristic acid (0.8 %), stearic acid (3.7 %), linolenic acid (0.3 %), and arachidic acid (0.1 %). If compared to the theory, palm olein contains lauric acid (0.1-0.2 %), myristic acid (0.9-1.0 %), palmitic acid (39.5-40.8 %), C16:1 (<0.2 %), stearic (3.9-4.4 %), oleic (42.7-43.9 %), linoleic (10.6-11.4 %), linolenic (<0.4 %) and arachidic acid (0.1-0.3 %) [5]. The FFA compositions of PO_o had been reported before [12]. It contains lauric acid (0.2 %), myristic acid (1.1 %), palmitic acid (35.7 %), stearic (3.5 %), oleic (45.4 %), linoleic (13.1 %) and linolenic (0.3 %). The separation of GC peaks was based on the carbon number and boiling point of each compound. The greater carbon number leads to longer retention time for the peak to be detected. Similar scenario happens to the FFA that had double bond on its structure because the double bond will increase the intermolecular force. By increasing the intermolecular force, the boiling point can be increased, therefore increasing the retention time.

Table 1. The Free Fatty Acid Compositions of PO_o

No.	Free Fatty Acid Type	Retention Time (minutes)	Relative Area (%)
1	Lauric acid	10.829	0.2
2	Myristic acid	14.689	0.8
3	Palmitic acid	19.518	36.3
4	Palmitoleic acid	20.187	0.2
5	Stearic acid	24.085	3.7
6	Oleic acid	24.895	47.7
7	N/A	25.581	0.2
8	Linoleic acid	25.986	10.4
9	N/A	27.515	0.1
10	Linolenic acid	27.773	0.3
11	Arachidic acid	28.558	0.1

Based on the HPLC analysis done, there were two major TAGs found which are POO (33.3 %) and POP (29.6 %) (Table 2). This is because of the major FFA of PO_o are oleic acid followed by palmitic acid. The separation of HPLC peaks was based on the equivalent carbon number (ECN) and the polarity of each TAG. Different ECN produces different based line of the peak. The greater ECN number, leads to shorter retention time. But, for the same baseline of TAGs, the less polar of TAG was firstly detected. The arrangement of TAGs is PLL (2.8 %), OOL (1.4 %), POL (12.4 %), PPL (7.3 %), OOO (3.6 %), POO (33.3 %), POP (29.6 %), SOO (2.6 %) and POS (3.8 %). The theoretical TAG compositions of palm oil are mainly contain of POP (27-31 %) and POO (20-26 %) [2]. Due to the fact that the palm oil had fractionised to produce PO_o, thus the TAG produced has higher olein. If compared to the HPLC analysis of PO_o done before, there were OLL (0.7 %), OOL (2.6 %), POL (14.8 %), PPL (10.2 %), OOO (5.5 %), POO (30.6 %), POP (18.0 %), SOO (3.3 %) [12].

Table 2. The Triacylglycerol (TAG) Compositions of PO_o

TAG Type	Equivalent Carbon Number (ECN)	Relative Area (%)
PLL	44	2.8
OOL	46	1.4
POL	46	12.4
PPL	46	7.3
OOO	48	3.6
POO	48	33.3
POP	48	29.6
SOO	50	2.6
POS	50	3.8

Physico-chemical characterisation

The physico-chemical of PO_o is shown in Table 3. The iodine value of PO_o is 61.67 whereas the acidity is 3.01 %. This acidity may happen during the storage and delivering time of the sample. The saponification value is 197.18 mgKOH/g and its average molecular weight of PO_o is 854.3 $gmol^{-1}$. PO_o contains 0.17 of unsaponifiable matter. This commercial oil only contains 0.22 % of water. The cloud point is 7 ^oC (± 1 ^oC) and the pour point is 5 ^oC (± 2 ^oC). Both fire and flash point were over 320 ^oC (± 5 ^oC). The oxidative stability by DSC was 179 ^oC. PO_o has kinematic viscosity about 45.9 cSt (40 ^oC) and 9.4 cSt (100 ^oC) with viscosity index of 195. PO_o was categorized as ISO VG 46 of viscosity grade [10]. Theoretically, the iodine value is not less than 55. Then, the cloud point was 7 – 10 ^oC. The saponification value was 194-202 and the unsaponifiable matter was less than 1.4 [2]. So, most of the characterizations of PO_o observed in this work are almost the same with the theoretical values. By referring to the flash and fire point, kinematic viscosity and viscosity index, it can be proposed that PO_o has the promising lubricant properties. Then, if compared with other ISO 46 commercialised samples which are Priolube 2065 and Priolube 2089 (Table 3) [13], some of the characterisations of PO_o were almost similar especially on the kinematic viscosity (40, 100 ^oC), viscosity index and flash point. But PO_o is still poor in its cloud and pour point. Priolube 2065 is the standard oleate base fluid for medium temperature application while Priolube 2089 is the medium temperature applications with superior low temperature properties [10].

Table 3. The Physico-chemical Properties of Palm Olein (PO_o)

Physico-chemical Test	Value $_{(exp.)}$	Priolube 2065	Priolube 2089
Iodine value	61.67	84	72
Acidity, %	3.01	0.20	0.05
Saponification value, mgKOH/g	197.18	-	-
Average molecular weight, $gmol^{-1}$	854.3	-	-
Unsaponifiable matter	0.17	-	-
Moisture content (Karl Fischer), %	0.22	-	-
Cloud point, ^oC	7 (± 1)	-21	-25
Pour point, ^oC	5 (± 2)	-51	-54
Flash point, ^oC	> 320 (± 5)	320	315
Fire point, ^oC	> 320 (± 5)	-	-
Oxidative stability (DSC), ^oC	179	-	-
Kinematic viscosity (40 ^oC), cSt	45.9	48	44
Kinematic viscosity (100 ^oC), cSt	9.4	9.8	8.7
Viscosity index	195	196	181
ISO VG Grade	ISO 46	ISO 46	ISO 46

By referring to Figure 1, the Stribeck curve has three types of lubricant conditions which are boundary, mixed and hydrodynamic lubricant. In the middle between mixed and hydrodynamic lubricant conditions, there is an elastohydrodynamic lubricant which shows that the friction coefficient decreasing during the increasing of parameter [14]. The comparison of tribological properties of PO_o at 40 ^oC and 100 ^oC is shown in Figure 2. PO_o exhibits low friction coefficient (min. 0.2 μ) at 40 ^oC, nonetheless, PO_o has recorded good friction coefficient (min. 1.2 μ) at 100 ^oC. This shows that PO_o have better lubrication properties even if the temperature is increased.

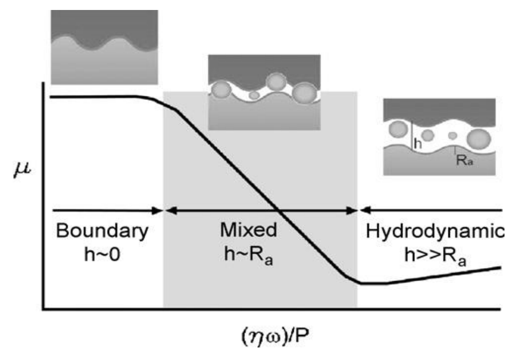

Figure 1. Sketch of a Stribeck curve relating friction coefficient; h: fluid film thickness, R_a: average surface roughness

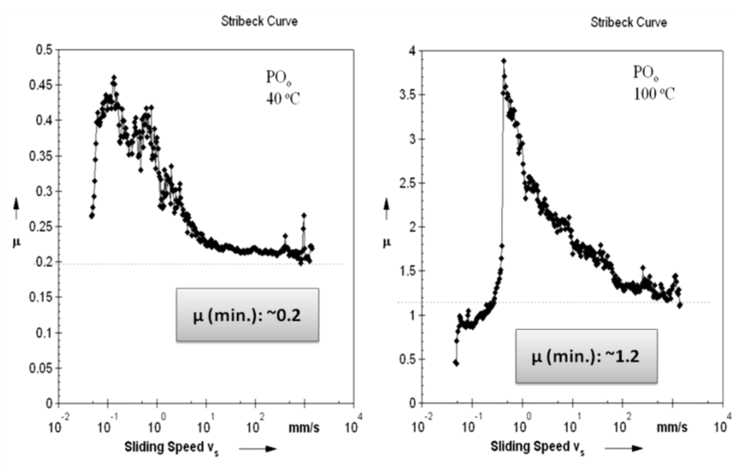

Figure 2. Comparison of Stribeck curves of PO_o at 40 ^oC and 100 ^oC

Conclusion

Based on the chemical compositions and lubrication analysis of palm olein observed in this research works, it is proven that it has potential to be developed as biolubricant base stock through some chemical modifications. PO_o can also be used directly as lubricant for medium temperature applications. The modifications used might improve some poor lubricating properties of palm olein.

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