

Tribological properties of palm oil bio-lubricant with modified carbon nanotubes

Izatul Hamimi Abdul Razak^{1,2}, Mohamad Ali Ahmad^{2,*}, Nadia Nurul Nabihah Ahmad Fuad², Khairul Syazwani Shahrudin²

¹Mechanical & Manufacturing Section, Universiti Kuala Lumpur Malaysia France Institute, 43650 Bandar Baru Bangi, Selangor, Malaysia

²Faculty of Mechanical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

*Corresponding author E-mail: mohama9383@salam.uitm.edu.my

Abstract

Vegetable oil has been identified to be the one of best replacement of mineral oil. Palm oil has also been used as replacement for current mineral oil apart from the application in domestic use. Its potential as based oil for hydraulic fluid, diesel engine, and lubricants has been confirmed in many previous studies. Additives are commonly added to lubricant oils with purpose to enhance the oil performance. Recent studies show that the size and quantity of additives used may play a big role in its tribological properties. Several studies reported that adding nanoparticles with the size between 1 to 100 nm into lubricating oil at certain weight percentage can reduce friction and improve anti-wear properties. Modification of lubricant oil with nanoparticle capable to give the sliding effect into rolling effect thus reduces surface contact and heat production. In the present work, carbon nanotube has been used as the Nano-additives in palm oil bio-lubricant. Four-ball tester was used to investigate its tribological properties under boundary lubrication (metal to metal contact). Result obtained shows that the addition of 0.04 wt% of carbon nanotubes recorded the lowest coefficient of friction with a 10.8% improvement compared to the pure palm oil. The additive also contributed to better wear scar diameters and possessed good anti wear properties for palm oil. This thus shows the significant potential of the carbon nanotubes as the wear preventive additive for palm oil bio-lubricant.

Keywords: Palm oil; Carbon Nano-tubes; Coefficient of friction; Wear; Extreme pressure.

1. Introduction

Palm oil is a well-known potential candidate in plant-based oil to replace the conventional mineral oil. Harvested all year round, the advantages and benefits initiate the palm oil to be used in varieties of application. Nowadays the utilization of palm oil as feedstock for bio-lubricants has been recognized in many studies [1, 2]. This is due to issues related to the depletion of world crude oil reserve, increasing crude oil prices and conservation of oil, which brought interest in the bio-based materials. Therefore, efforts have been placed with emphasis to develop a renewable, biodegradable, and environmentally friendly industrial fluids, or lubricant.

Lubricant plays a significant role in a tribology system in order to enhance the reliability and service life of friction units. Not only expected to perform as anti-friction media, it also should be able to facilitate smooth operations, reduce wear and heat loss from moving contact surfaces, prevent rust and reduces oxidation as well as act as seal against dirt, dust and water [3, 4].

Increasing demands for lubricant in present and future consumptions are in line with current technological growth. This brings to the development of alternatives for current industrial lubricants, particularly mineral and crude oils, in order to meet the future demands. In recent time, there are high growing interests in the alternative bio-lubricants derived from vegetable based. Numerous development and research have been carried out to explore the potential of vegetable oils to perform effectively as petroleum-

based lubricants in ranges of applications including in automotive, metal working, machineries and others. However, due to the limited capabilities of vegetable-based oils in terms of poor cold flow properties and oxidation stability [5, 6], several methods have been adopted in order to improve the performance. The addition of several types of additives may also improve the friction reduction and anti-wear properties of the oils.

The use of nanoparticles in vegetable lubricant as oil additives have extensively being studied in this past few years with main purpose to improve the oil properties. Metal-based, metal oxide, metal composite, boron-based and carbon-based nanoparticles are the five major groups of nanoparticles that usually added to lubricant [7]. The addition of few types of nanoparticles such as copper oxide (CuO), Molybdenum di sulfide (MoS₂), Titanium Oxide (TiO₂), Zink Oxide (ZnO), graphite, graphene, and other metallic nanoparticles into the vegetable oils have proven the good contribution to wear and friction reductions [8–11]. This is due to the fine size of the nanoparticles which normally less than 100 nm allows it been easily deposited on the friction surfaces and forms a protective deposit film. Thottackkad et. al. [12] found that an optimum concentration of nanoparticles may improve the coefficient of friction and the specific wear rate. The study was carried out on the tribological properties of coconut oil with addition of CuO nanoparticles as additive. The authors also studied the optimum concentration of the additive. Kiu et al. [7] on his study was added graphene nanoparticles as additives to palm oil and found a significant improvement in the reduction of friction coefficient and wear scar diameter.

Carbon nanotube is another alternative for lubrication additive which gain more attention among researchers nowadays. The tube-shape material is basically made of carbon with nano-scale diameter. As a novel nanostructure that derived by bottom-up chemical synthesis approaches, nanotubes are among the strongest and most resilient materials known to exist in nature [13]. According to Odom et al. [14], nanotubes have the simplest chemical composition and atomic bonding configuration but exhibit the most extreme diversity and richness among nanomaterials in structures and structure-property relations. There are many different types of carbon nanotubes which normally categorized as either single-walled (SWNT) that have a regular straw shape as show in Fig. 1, or multi-walled nanotubes (MWNT). The ability of the carbon Nano-tubes in enhancing tribological properties of contact surfaces have been discussed in few past studies, which the friction reduction and anti-wear ability of a base lubricant have been effectively improved. It was attributed from the good disperse-ability of the modified carbon nanotubes [15, 16].

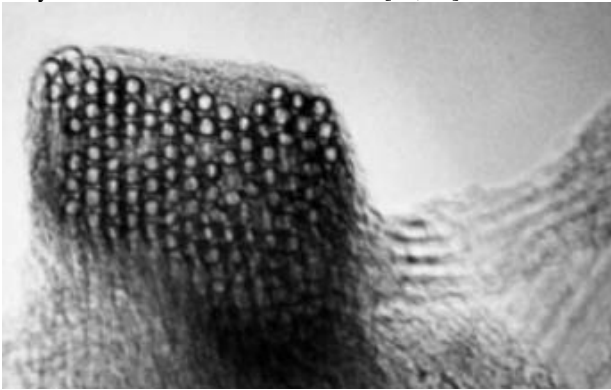


Fig. 1: The cross-section of a bundle of SWNTs [13]

In the present study, the carbon nanotube (CNT) optimum weight percentage (wt%) was utilized as an additive in palm oil bio-based lubricant and the tribological properties were investigated. The different wt% concentration amount of the carbon nanotubes was tested and the ability in friction and wear characteristic was analysed.

2. Experimental setup

2.1. Sample preparation

Single-walled carbon nanotube (>70% TGA) as oil additive was mixed with palm oil as base oil and shaken by using an ultrasonic vibrator to ensure homogeneous dispersion of mixture without agglomeration. Properties of the palm oil are listed in Table 1. Eight samples were prepared for the testing specimens, which are palm oil without any additive and palm oil mixed with carbon nanotube particle at 0.02 %, 0.03 %, 0.04 %, 0.05 %, 0.06 %, 0.07 % and 0.08 % of weight percentages. The carbon nanotubes were supplied by Sigma Aldrich Ltd.

Table 1: Palm oil properties

Properties	
Density (g/ml)	0.9081
Kinematic viscosity at 40°C (mm ² /s)	43.86
Kinematic viscosity at 100°C (mm ² /s)	8.72
Viscosity index	182
Total acid number (mg KOH/g)	6.35

2.2. Tribology testing

A four-ball friction and wear tester produced by Koehler Instrument Company, Inc., was used to study the tribological properties of carbon nanotubes as vegetable based oil additive. The purpose of the four-ball wear test in this study is to test the wear preventive (WP) and extreme pressure (EP) properties of a lubricant. In the WP test, the lubricant's coefficient of friction and the wear scar

diameter when sliding actions between the balls with certain load can be measured. Whereas, EP measures the load carrying capability of a lubricant and the relative ability to prevent wear under such applied loads.

The series of tests were conducted in accordance with ASTM D4172 (WP) [17] by four ball friction and wear tester equipment, with different concentration amount of carbon nanotubes additive. A new set of four steel balls (AISI 52100) was used for each set of tests with 14.7 mm ball mean diameter and hardness range between 61 to 63 HRC. These balls were thoroughly cleaned with n-Heptane and dried prior the test set up. The three stationary balls then been clamped into the ball pot and the forth ball was held in a rotating spindle. A sample volume of approximately 10 ml lubricant was poured into the ball pot assembly for each test. Fig. 2 illustrates the four-ball assembly installed in the wear tester equipment. After the completion of the test, wear scar on the contact surfaces of balls was then observed under a digital optical microscope.

The EP test was conducted in accordance with ASTM D2783 standard [18], using the same equipment as in WP test. Only palm oil with the optimum concentration of CNT, which producing minimum coefficient of friction was tested. The data was compared with palm oil without any additive. Initially, 24 kg of load was applied, and the load was gradually increased for about every 10 s until the balls were welded. The wear scar diameter on the balls was measured for each load to monitor the wear growth. The summary of test parameters for the WP and EP tests are listed in Table 2.

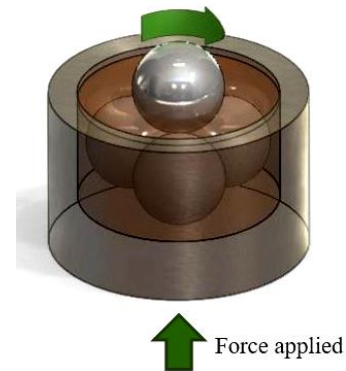


Fig. 2: The four-ball assembly

Table 2: Four ball tester parameters according to ASTM standard

Parameter	WP (D4172)	EP (D2783)
Rotating Speed	1200±60 rpm	1760±40 rpm
Load	40±2 kgf	As per standard
Duration	60±1 min	Series of 10 sec
Temperature	75±2 °C	18 to 35°C
Based Oil	Palm Oil	Palm Oil
Additives	Carbon nanotube	Carbon nanotube
Concentrations	0.02 to 0.08 % wt	Optimum % wt

3. Result and discussion

3.1. Influence of carbon nanotubes on friction and WP (wear preventive) properties

Carbon nanotubes (CNT) in the range of 0.02-0.08 wt% concentrations were added in commercial palm oil and the friction and wear properties were analysed. The average friction coefficient of the palm oil added with the different concentrations of CNT is depicted in Fig. 3. It shows the variation of coefficient of friction of the palm oil without additive and with seven concentrations of CNT additive. Coefficient of friction of the palm oil without additive was about 0.074. The small volume addition of carbon nanotubes in palm oil however caused slightly reduction of the coefficient of friction to 0.073. The minimum changes might due to very small amount of CNT applied which not really effect the friction

between surfaces. The coefficient of friction value yet reduced to 0.067 with the addition of 0.04 wt% of CNT, recorded the lowest coefficient of friction among the other samples with a 10.8% improvement compared to the pure palm oil. In this condition, the nanoparticles provided a thin lubrication film on the surfaces and minimize friction at the sliding interfaces.

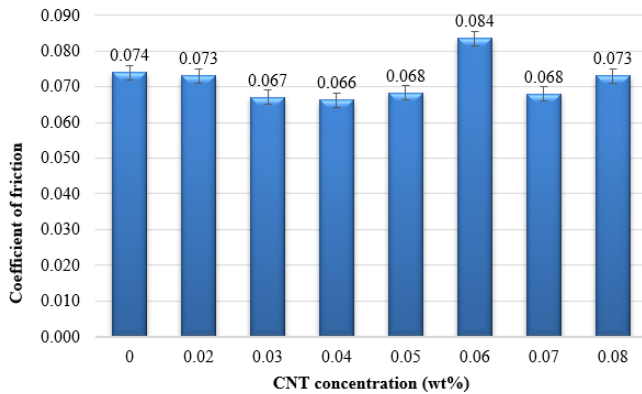


Fig. 3: Average coefficient of friction of palm oils with carbon nanotubes additives

The similar finding was also obtained by Kiu et al. [19] whose demonstrated the reduction in friction coefficient and wear when carbon nanotubes was added in the studied vegetable oil. In addition, according to Cornelio et al. [20], the positive effect on lubricant properties by the addition of CNT is might be due to the high elastic modulus of the CNT which reducing the metallic contact between surfaces and leads to reduction of adhesive wear and friction coefficient. The authors added that, if higher contact pressure is applied, the carbon nanotubes can deform and forms a lamellar solid on the contact surfaces. Further addition of CNT to 0.06 wt% however causes the coefficient of friction increases to 0.084. This is due to the high concentration of nanoparticles which increase stress concentration on contact surfaces and leads to abrasive wear [21]. In other word, the high concentration of the CNT leads to stacking and agglomerations of the particles which cause additional rubbing between contact surfaces. Thus this contributes to higher friction and wear. In addition, it might also contribute by low disperse of the CNT particles in palm oil.

Ball surface investigation by optical microscopy shows the different wear surface and scar diameter when the carbon nanotubes additive was included in palm oil. Fig. 4 tabulated the average wear scar diameter for the palm oil with various concentration of CNT additive. Wear scar diameter is damaged on the balls contact surfaces due to the material removal during sliding contact.

The significance improvement in wear scar diameter was found for palm oil with 0.03 wt% of CNT, at 0.682 mm which is about 5.1% reduction compared to palm oil without additive. This shows that the CNT possess a good anti-wear behaviour with minimal concentration. Although the optimum concentration of the CNT additive (0.04 wt%) showing higher wear scar diameter, yet it still better as compared to the pure palm oil with about 2.4% improvement. From the observation of the wear scar, further increasing of CNT concentrations will increase the scar diameter. This can be explained that an increase concentration of CNT causes higher number of nanotubes particles in contact between the balls and rubbed between each other.

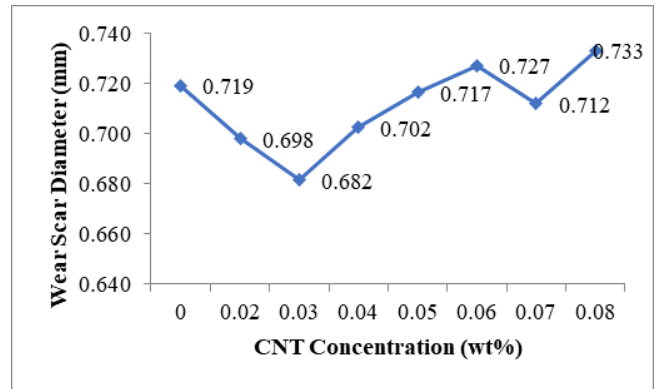


Fig. 4. Average wear scar diameter of palm oils with carbon nanotubes additives

The optical micrograph images of the ball specimen wear scars are illustrated in Fig. 5. Wear scar produced with palm oil without additive is presented in Fig. 5(a), showing the not very smooth yet clean surface. Observing the wear scar produced with palm oils with the solid additives, the presence of CNT particles can be seen on the scratch groove surfaces. The scattered CNT particles was observed in Fig. 5(c) for the palm oil with 0.03 wt% CNT, and a smoother scar edges was produced. The particles might contribute to less friction between the contact surfaces and producing lower coefficient of friction and wear scar size. This was supported by Gulzar et al. [1] who claimed that the precipitation of nanoparticles on the contact surface contributing to the smooth surface.

3.2. EP (Extreme pressure) characterization

Parameters summary of for extreme pressure (EP) test was tabulated in Table 2. Under extreme pressure, two samples were tested; palm oil without additive and palm oil with 0.04 wt% of CNT, as it was the optimum concentration (as referred to the lowest coefficient of friction). About 20 kg of load was applied for every 10 s operation and added gradually until the final seizure load was reached. At this point, the oil film developed on the ball surfaces have totally breakdown and the four balls specimen weld with each other [22]. The average wear scar diameters produced at the balls' contact surfaces are depicted in Table 3, focusing only the scars on the high applied load. The results imply that the palm oil with and without the CNT additive have the same ability to retain its properties up to 100 kg of load, before seizure at 126 kg load. Nano-particles in general have good ability in modifying the friction ability of base oil and less influencing the oil properties. The nanoparticles also might not disperse completely in the base oil. Thus, this might because the CNT nanoparticles have insufficient ability to provide resistance to extreme pressure.

The wear scar diameter for palm oil with CNT additive however was reduced to 26.2% at 80 kg load. Yet at 100 kg load, the wear scar diameter was almost no different even with the utilization of CNT. According to Lin et al. [23], the extreme pressure (EP) additives performance are relied on three main factors; the tribo-film strength, the additives-surface reaction rate, and the base oil-additive compatibility. Result obtained in this study revealed that the CNT additive has less compatibility with palm oil in improving the EP characteristic. This is due to the properties of solid particles that unable to change the chain between elements in the palm oil lubricant, which maintaining the oil's EP properties.

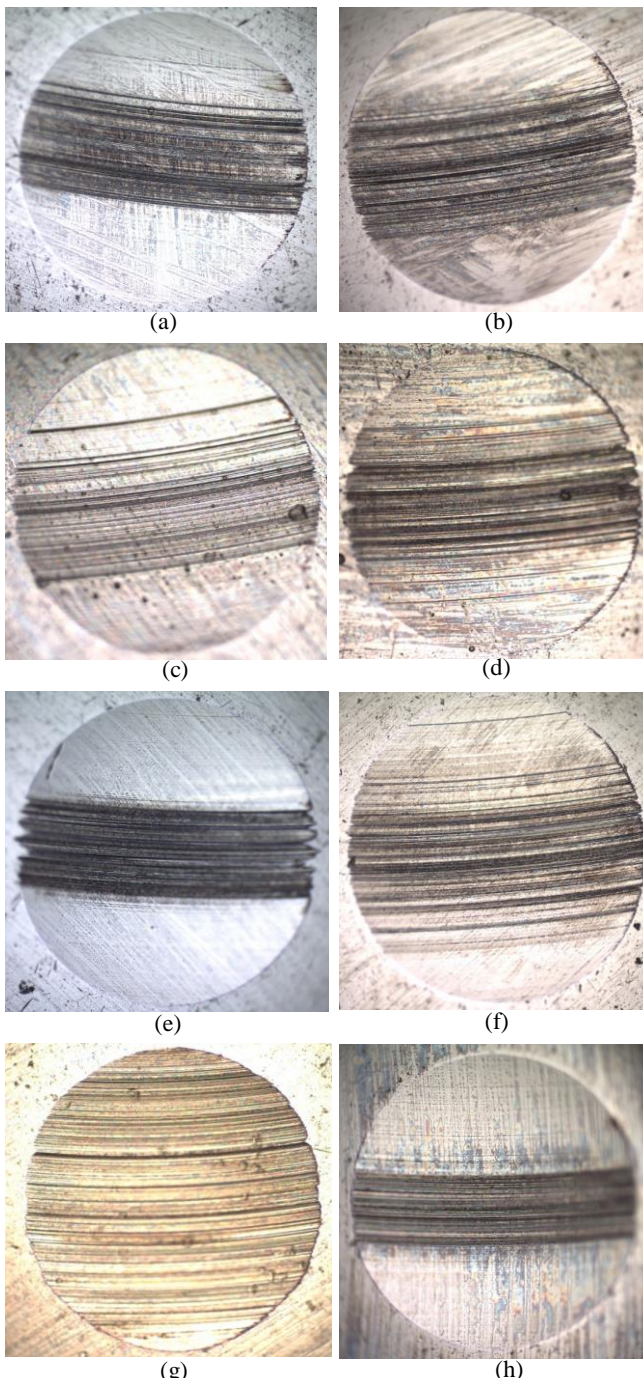


Fig. 5: Optical micrograph of wear scars for palm oils with CNT concentration (magnification 200X): (a) 0 wt%, (b) 0.02 wt%, (c) 0.03 wt%, (d) 0.04 wt%, (e) 0.05 wt%, (f) 0.06 wt%, (g) 0.07 wt% and (h) 0.08 wt%.

Table 3: Wear scar diameters for EP test

Load (kg)	Avg. wear scar diameter (mm)	
	80	100
Palm Oil	0.58	2.608
Palm Oil with CNT (0.04 wt%)	0.428	2.64

4. Conclusion

This current work has focused on the preliminary development of a bio-lubricant using palm oil with the addition of carbon nanotubes. The tribological properties of carbon nanotubes as bio-lubricant additive were investigated with the aid of a four ball wear testing machine. The testing results present a significant improvement in the palm oil properties with the reduction of friction coefficient and wear scar diameter. It was proven that the addition 0.04 wt % of carbon nanotubes may improve the friction

coefficient by 10.8% as compared to the palm oil without additive. Under extreme pressure condition, the maximum load bearing capacity was remaining same at 100 kg even with addition of carbon nanotubes. In overall, it can be concluded that the addition of carbon nanotubes in palm oil have a great potential as an alternative to the current commercial mineral oil due to the improved tribological properties.

Acknowledgement

The authors would like to express gratitude to Institute of Research Management & Innovation (IRMI) of Universiti Teknologi MARA for the Research University Grant, LESTARI (087/2017), Faculty of Mechanical Engineering UiTM, and Ministry of Higher Education, Malaysia for their support.

References

- [1] Gulzar M, Masjuki HH, Varman M, Kalam MA, Mufti RA, Zulkifli NWM, Yunus R, and Zahid R (2015), Improving the AW/EP ability of chemically modified palm oil by adding CuO and MoS nanoparticles. *Tribology International*, 88, 271–279.
- [2] Heikal EK, Elmelawy MS, Khalil SA, and Elbasuny NM (2017), Manufacturing of environment friendly biolubricants from vegetable oils. *Egyptian Journal of Petroleum*, 26(1), 53–59.
- [3] Mobarak HM, Niza Mohamad E, Masjuki HH, Kalam MA, Al Mahmud KAH, Habibullah M, and Ashraful AM (2014), The prospects of biolubricants as alternatives in automotive applications. *Renewable and Sustainable Energy Reviews*, 33, 34–43.
- [4] Panchal TM, Patel A, Chauhan DD, Thomas M, and Patel JV (2017), A methodological review on bio-lubricants from vegetable oil based resources. *Renewable and Sustainable Energy Reviews*, 70 (October 2015), 65–70.
- [5] Gapinski RE, Joseph IE, and Layzell BD (1994), A vegetable oil-based tractor lubricant, *SAE Tech Paper* 941785, pp. 1–9.
- [6] Erhan SZ, Sharma BK, and Perez JM (2006), Oxidation and low temperature stability of vegetable oil-based lubricants, *Industrial Crops and Products*, 24, 292–299.
- [7] Kiu SSK, Yusup S, Soon CV, Arpin T, Samion S, and Kamil RNM (2017), Tribological investigation of graphene as lubricant additive in vegetable oil, *Journal of Physical Science*, vol. 28, 257–267.
- [8] Zulkifli NWM, Azman SSN, Kalam MA, Masjuki HH, Yunus R, and Gulzar M (2016), Lubricity of bio-based lubricant derived from different chemically modified fatty acid methyl ester, *Tribology International* vol. 93, 555–562.
- [9] Zen AG and Rashmi GW (2013), Tribological Evaluation of Nano Graphene Platelets as an Additive to Biolubricant Base Fluid, *EURECA*, 10–11.
- [10] Zulkifli NWM, Kalam MA, Masjuki HH, and Yunus R (2013), Experimental analysis of tribological properties of biolubricant with nanoparticle additive., *Procedia Eng.*, vol. 68, 152–157.
- [11] Su Y, Gong L, and Chen D (2015), An Investigation on Tribological Properties and Lubrication Mechanism of Graphite Nanoparticles as Vegetable Based Oil Additive, *J. Nanomater*, September, 1–7.
- [12] Thottackkad MV, Perikinalil RK, and Kumarapillai PN (2012), Experimental evaluation on the tribological properties of coconut oil by the addition of CuO nanoparticles, *International Journal of Precision Engineering and Manufacturing*, vol. 13, no. 1, 111–116.
- [13] Dai HJ (2002), Carbon nanotubes: opportunities and challenges, *Surface Science*, vol. 500, no. 1–3, 218–241.
- [14] Odom, TW, Huang JL, Kim P, and Lieber CM (1998). Atomic structure and electronic properties of single-walled carbon nanotubes. *Nature*, 391(6662), 62–64.
- [15] Chen CS, Chen XH, Xu LS, Yang Z, and Li WH (2005), Modification of multi-walled carbon nanotubes with fatty acid and their tribological properties as lubricant additive, *Carbon*, vol. 43, no. 8, 1660–1666.
- [16] Pei X, Xia Y, Liu W, Yu B, and Jing (2008), Polyelectrolyte-Grafted Carbon Nanotubes: Synthesis, Reversible Phase-Transition Behavior, and Tribological Properties as Lubricant Additives, *Journal of Polymer Science. Part A: Polym. Chem.*, vol. 46, 7225–7237.
- [17] ASTM4172-94 Standard test method for wear preventive characteristics of lubricating fluid (four-ball method). West Conshohocken, PA: ASTM International; 2009.

- [18] ASTM2783-03 Standard test method for measurement of extreme-pressure properties of lubricating fluid (four-ball method). West Conshohocken, PA: ASTM International; 2004
- [19] Kiu SSK, Yusup S, Chok VS, Taufiq A, Kamil RNM, Syahrullail S and Chin BLF (2017), Comparison on tribological properties of vegetable oil upon addition of carbon-based nanoparticles, *IOP Conference Series: Materials Science and Engineering*, vol. 206, no. 1.
- [20] Cornelio JAC, Cuervo PA, Hoyos-palacio LM, Lara-romero J and Toro A (2016), Tribological properties of carbon nanotubes as lubricant additive in oil and water for a wheel – rail system, *Journal of Materials Research and Technology*, vol. 5, no. 1, 68–76.
- [21] Talib N, Nasir RM, and Rahim EA (2017). Tribological behaviour of modified jatropha oil by mixing hexagonal boron nitride nanoparticles as a bio-based lubricant for machining processes. *Journal of Cleaner Production*, 147, 360–378.
- [22] Zulkifli NWM, Kalam MA, Masjuki HH, Shahabuddin M, and Yunus R (2013). Wear prevention characteristics of a palm oil-based TMP (trimethylolpropane) ester as an engine lubricant. *Energy*, 54, 167–173.
- [23] Lin YC, Cho YH, and Chiu CTe. (2012). Tribological Performance of EP Additives in Different Base Oils. *Tribology Transactions*, 55(2), 175–184.