



## Effect of tert-butylhydroquinone on tribological performance of palm oil lubricant and aluminium plate using linear reciprocating tribometer

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KEYWORDS	ABSTRACT
<p>Tert-butylhydroquinone Palm oil lubricant Aluminum Bio lubricant Coefficient of friction Wear</p>	<p>The tribological performance of palm oil lubricants with Tert-Butylhydroquinone (TBHQ) on aluminium was investigated with palm oil PO between temperatures of 40°C and 100°C using Linear Reciprocating Tribometer LRT ASTM G133. TBHQ in concentrations by wt.% of 0.1, 0.2, 0.3 and 0.4 were separately dispersed into PO to examine its effect on tribological performance, oxidation onset temperature and viscosity index. PO with 0.3 wt.% of TBHQ presented coefficients of friction COF of 0.063, 0.068, 0.083 and 0.11 at 40°C, 50, 75°C and 100°C respectively. Also, commercial lubricant Shell T46 oil gave COF of 0.063, 0.066, 0.086 and 0.095 while the original PO without TBHQ inclusion showed COF of 0.073, 0.081, 0.095 and 0.12 under same conditions. Meanwhile, 0.3 wt.% TBHQ showed similarities with COF of T46 as a benchmark lubricant. Even though aluminium wear in PO reduced significantly at higher load and temperature due to TBHQ addition, it however showed no significant reduction effect in wear between 40°C and 60°C for the 60N load. Greater wear reduction under 80N load and 100°C between 25% - 67% was observed. The addition of TBHQ to PO also enhanced its oxidation onset temperature upwards by 21.8% from 178.5°C to 217.5°C.</p>

## 1.0 INTRODUCTION

The need to abate the increasing concerns over environmental pollution and degradation due to continued usage of non-degradable mineral oils for lubrication in transportation, industrial and engineering applications has dominated the research space in recent times. Finding a suitable lubricant for these applications and many other new inventions has intensified researchers' quest in that direction (Ganesh & Prabhu, 2022). Reddy et al. (2014) in varying proportions by percentage volume of palm oil blended with base mineral oil SAE20W recorded appreciable emission performance of a 4-stroke Contact Ignition (CI) engine. Their study showed that, compared to mineral-based commercial oil, palm oil-based lubricants showed improved tribological properties in friction and wear reduction. Masjuki & Maleque (1997) carried out a comparative study of wear, friction, viscosity, lubricant degradation, and exhaust emissions with palm oil and commercial lubricating oil using the four-ball tester. Their results revealed that palm oil-based lubricating oil exhibited better performance in terms of wear and friction than the commercial oil. However, palm oil-based lubricants were more effective in reducing the emission levels of CO and hydrocarbon.

Beyond this, many other researchers have worked on palm oil and some other vegetable oils in prospecting biodegradable lubricants. Dandan & Syahrullail (2017) demonstrated that palm oil can be applied for lubrication in sensitive operations due to their non-toxicity. Distinct lubricity of palm oil at low temperature is a potential for its preference upon other vegetative seed oils (Singh et al., 2018, 2020). Unfortunately, the problem of poor oxidation stability and low flow property of palm oil at low temperature limits the potential for palm oil as a lubricant (Dandan & Syahrullail, 2017). This menace has aroused research interests towards improving viscosity index (VI) by modifications in the structure and reactivity. Most of the modifications that have been done include esterification (Zulkifli et al., 2013), transesterification (Thaoklua et al., 2018), fractionation, prefractionation, addition of nano-additives (Hamdan et al., 2018; Shaari et al., 2015), addition of antioxidant (Liu et al., 2022), addition of surfactants (Patti et al., 2021), polymerization (Ashok et al., 2017) etc. Another method that has been applied is by improvement in the properties of the tribo-pair materials requiring lubrication. Tribological properties of the materials as well as the mechanical and physiological properties were improved by different methods ranging from heat treatment (Reis et al., 2022), reinforcement and nano addition (Pichumani et al., 2018; Reis et al., 2022). The overall objective of the modifications is to increase the load bearing capacity of the tribo-pairs against wear, attrition, corrosion and other forms of material erosion (Beheshti et al., 2020). Ammarullah et al. (2023) evaluated the deformation and wear particles from hard-on-hard bearing couple and hard-on-soft bearing couple applications in hip prosthesis under simulated walking conditions. Their comparison of running-in-linear and volumetric wear showed less deformation in the hard-on-hard bearing couple. Their model exhibits lower running-in-linear and volumetric wear. However, apart from applications in medicine, preferable choices of tribo-pairs could be limited by cost, unavailability of technical know-how and order uncertainties. In such situations, modifications and adaptation of the available tribo-pair for effective and optimal performance are required.

This study examined the effect of Tert-Butyl Hydroquinone TBHQ addition on the tribological performance of palm oil lubricants with aluminum plate-steel ball tribo-pair, using the Linear Reciprocating Tribometer LRT, ball on flat mechanism. TBHQ is a synthetic antioxidant frequently used in food processing to increase shelf life, control oxidation and rancidity in oils and fats. It functions by preventing the production of free radicals, which can lead to food spoilage and deterioration. TBHQ has also been applied to enhance tribological performance of certain mineral

and bio-lubricants under varying conditions (Liu et al., 2016; Sapawe et al., 2016). Results of certain efforts have indicated that lubricants' performance could be enhanced by dispersing TBHQ into lubricant (Ojaomo et al., 2023) (Liu et al., 2016) (Sapawe et al., 2016). Aluminium alloys have gained prominence in different engineering applications such as marine, aerospace, defense and automotive sectors, due to their light weight, better ductility, good conductor and low cost (Jurwall et al., 2023) (Gill et al., 2022). However, its softness and malleable properties make it prone to scratches and high abrasive wear, necessitating use of lubricants to minimize material loss due to friction during operation (Nuraliza et al., 2016) (Ukachi & Ojaomo, 2018). Meanwhile the increasing concerns for environmentally friendly and biodegradable lubricants to reduce environmental degradation from use of fossil oil-based lubricants have also continued (Thaoklua et al., 2018). Palm oil lubricants have been shown to indicate good lubricity, non-toxicity and environmentally friendly but with limitations of low range of viscosity and poor oxidation stability (Dandan & Syahrullail, 2017). Even though TBHQ has been shown to reduce friction and wear in vegetable oil-based lubricants on steel- tribo-pairs according to Zulhanafi et al. (2019) and Ojaomo et al. (2023), its effects on palm oil lubricants in a steel-aluminium tribo-pair require more understanding. The objective was to determine the tribological effects of the varied TBHQ concentration on the tribo-pair in palm oil lubricant. Effects of the optimum concentration on the coefficient of friction COF, viscosity index VI, oxidation onset temperature OOT and aluminium wear loss WL were examined.

## 2.0 MATERIALS AND METHODS

### 2.1 Linear Reciprocating Tribometer

Linear Reciprocating Tribometer LRT Winducom 2010 ASTM G133 test rig Figure 1(a) and (b) was used for the experiment. Figure 1(a) showed the pictorial view while Figure 1(b) showed the schematic diagram of the operation mechanisms. LRT is set up according to standard ASTM G133 for friction and wear behavior under reciprocating sliding conditions (Chaudhary et al., 2020). LRT is fitted with data acquisition system to record data for the coefficient of friction COF in real-time on the computer. It consists of an oil bath for lubricant samples and for holding the 20 mm<sup>2</sup> flat aluminium plate sample in fixed unmovable position. It has a movable reciprocating jaw that holds the 10 mm diameter steel ball under specified load which presses it against the plate. The tribometer operated by repeatedly sliding the steel ball bearing to-fro on a fixed aluminium plate with 10mm stroke in the oil bath for 30 minutes. The loads varied between 40N to 100N and repeated for the varying concentrations of TBHQ in PO. Each sample was repeated three times, and their average values were determined.

### 2.2 Dispersion of TBHQ

Palm oil PO was purchased from Sigma Aldrich Inc., a Malaysian online chemical store (Norfazilla et al., 2018). Shell Turbo T46 ISO-32 (T46) was supplied by shell Oil Inc Malaysia. Shell T46 was used as synthetic benchmark mineral oil to compare the results of wear and friction due to its characteristic wide areas of application. Shell T46 is formulated from high quality hydrogenated base oil and a combination of zinc-free additives that provide excellent oxidation stability against rust, corrosion and foaming. Table 1 shows the properties of SAE20W40, PO and Shell T46. The choice of T46 in applications where strong control over rust and oxidation is required formed the basis of its preference for this study. Whereas SAE grades are indicated for

crankcase engines. Also, TBHQ was supplied by IOI Loaders Croklaan based in Pasir Gudang. Different concentrations of TBHQ were prepared in ratios 0.1; 0.2; 0.3 and 0.4 wt.% of TBHQ to PO. To prepare modified PO lubricant with TBHQ concentration of 0.1 wt.%, 0.30g of TBHQ was weighed using electronic weighing balance ASTM E898-20 and dispersed into 300g of PO through vigorous mechanical agitation using IKA Digital Ultra Torax T25 Homogenizer shown in Figure 1(d) which was rotated at speed of 10000 revolution/minute for 1 hour. Likewise, concentrations of 0.2; 0.3 and 0.4 wt.% were dispersed in the same manner (Hassan et al., 2016). The aim was to blend TBHQ with PO in preparing the modified PO with enhanced antioxidant properties to promote anti-oxidation strength of PO (Sapawe et al., 2016) (Zulhanafi et al., 2019).

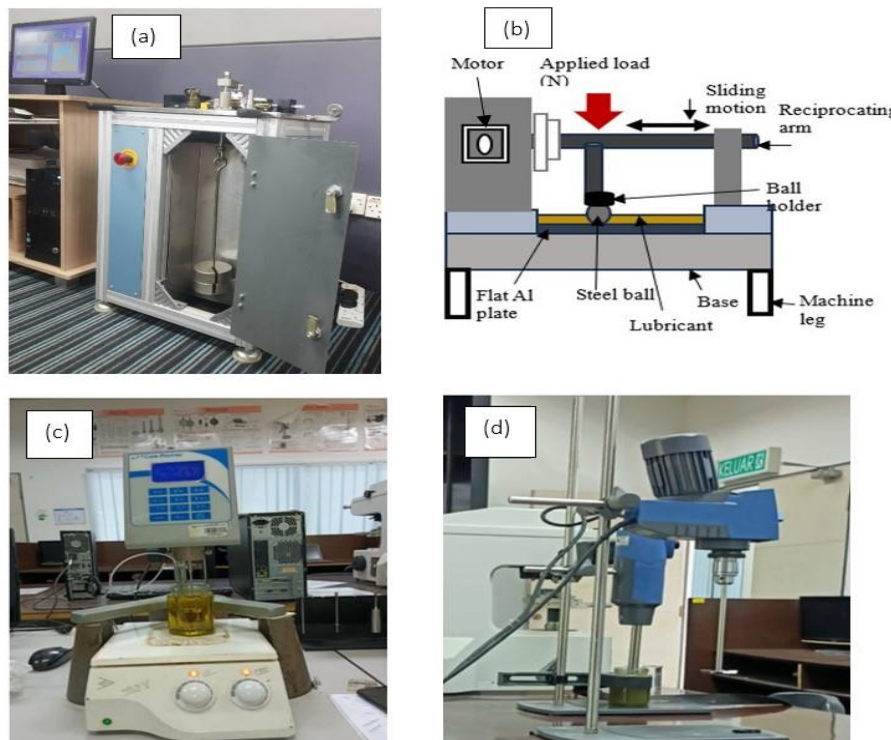


Figure 1: Apparatus used for experiments: (a) LRT pictorial view (b) Schematic diagram of LRT operation mechanism (c) Viscometer (d) Homogenizer.

Table 1: Properties of oil samples.

Oil	Viscosity at 40 °C	Viscosity at 100 °C	Viscosity index VI	Density g/cm <sup>3</sup>	Pour point °C maximum	Flash point °C
Shell T46	46.0	6.9	105	0.858	-27	220
Palm oil	40-24	7.9	188-210	0.865	9	280
SAE20W40	120	14-16	110	0.855	-21	220

### 2.3 Tribological Performance of Different Concentrations

The LRT was applied to carry out tribological tests of the prepared concentrations one after the other. To examine the most suitable concentration amongst the selected variations in terms of reduced coefficient of friction COF and wear WL due to each modified PO with TBHQ concentration in different wt.%. Test standard ASTM G133 was used due to the orientation of aluminium plate and the steel ball tribo-pair which requires ball on flat tribometer test rig (Marjanovic et al., 2006). Test parameters are load: 40-100N; frequency: 5Hz; Stroke: 10 mm; Temperature: 50 °C, 75 °C and 100 °C. Different concentrations of TBHQ uniformly dispersed into PO were 0.0%wt, 0.1%wt, 0.2%wt, 0.3%wt and 0.4%wt (Hao et al., 2020) (Thirugnanasambantham et al., 2020).

The aluminium plate was weighed before operation and after on LRT with four-digit chemical weighing balance ASTM E898-20 according to Pichumani et al. (2018). The wear loss WL was measured by weighing the aluminium plate before and after each experiment to deduce loss in weight (Nuraliza et al., 2016). Likewise, modified 0.3 wt.% TBHQ+PO, PO and T46 oils were run on LRT to determine their respective WL values under 60N and 80N loads at temperatures between 40 °C and 100 °C. Each test was repeated three times and the average values determined were compared. Precautions were taken by cleaning the aluminium plate with acetone to eliminate presence of oil and wear debris from the aluminium plate before each weight measurement.

### 2.4 Viscosity Index

Viscometer was used to measure the kinematic viscosity of PO only and that of 0.3 wt.% TBHQ blend with PO at 40 °C and 100 °C to determine the viscosity indexes of modified PO with TBHQ according to ASTM D 445 and ASTM D2270 (Verdier, 2009). Figure 1c shows the experiment for the kinematic viscometer measurement. A 250ml beaker containing PO was placed on the electric heater and stirred continuously with a rotating viscometer according to kinematic viscometer test standard ASTM D 445. The test was repeated for 0.3 wt.% TBHQ+PO and T46 oils. The viscosity indexes VI correlating to the kinematic viscosities of the respective samples were determined based on ASTM D2270. VI of 0.3wt.% TBHQ+PO, PO and T46 were compared with the original PO before TBHQ inclusion.

### 2.5 Oxidation Onset Temperature

To enhance the capacity of PO with potential for engine lubrication, TBHQ addition to PO was examined for degradation using differential scanning calorimetry to determine the oxidation onset temperature OOT as presented in previous literature (de Jesus et al., 2020). Even though specific oil formulations are meant for specific purposes in their applications (Budilarto & Kamal-Eldin, 2015). Differential scanning calorimetry DSC ASTM 3418 analysis was conducted with inclusion of antioxidant TBHQ in PO performed with a Q-100 TA instrument, using 5–10mg samples sealed in hermetic aluminum pans (Focke & Westhuizen, 2010). Cooling and heating rates of 10 °C/min were applied with advantage of being fast with greater data repeatability in line with previous presentation (Zulhanafi & Syahrullail, 2019). The flow rate of 50ml/min was applied from 25 °C. up to 350 °C. The oil was poured into a pressure vessel with a copper coil as a catalyst and then pressurised by oxygen gas at 90 psi (0.62 MPa).

### 3.0 RESULTS AND DISCUSSION

#### 3.1 Tribology Tests

The LRT data was generated real-time by the system data acquisition software which was analyzed by graphs of coefficients of friction COF at specified loads as shown in Figure 2. The COF was investigated under a load of 80N, 60N, and temperatures from 40 °C to 100 °C. Figure 2 and Figure 3 clearly showed the effects of TBHQ inclusion in PO on their COF and weight loss WL respectively. Figure 2 showed that PO without TBHQ was indicated as 0.0 wt.% TBHQ while PO with TBHQ inclusions by concentrations of 0.1%wt, 0.2%wt, 0.3%wt and 0.4%wt. It further showed that after 30 minutes of running the LRT experiment under load of 60 N and temperature of 55 °C. The oil sample with 0.0 wt.% of TBHQ (without TBHQ) has an average COF value of 0.143. Other TBHQ concentrations of 0.1 wt. %, 0.2 wt.%, 0.3 wt.% and 0.4 wt. % had their average COF values as 0.125; 0.111; 0.103 and 0.195 respectively as seen in Figure 2.

The commercial mineral oil T46 as benchmark lubricant has an average COF of 0.117. The result showed a range of values with increment in the amount of TBHQ causing corresponding decrease in COF until the COF marginally rose beyond the sample without TBHQ presence. As shown in Figure 4, the highest value of COF was observed in sample 0.4 wt.% This could be due to the quantity of TBHQ solute which might form grit particles in the oil leading to possible agglomeration between the film layer of oil. This is because other dispersed TBHQ concentrations were observed to be uniformly dissolved in PO in all concentrations except the 0.4 wt.% in which the solutes were seen as sediments below the containing bottle after being left to settle overnight. Invariably, it could possibly promote agglomeration of particles and increased wear.

Similarly, this may likely cause increased coefficient of friction as seen in Figure 2 and Figure 3. On the other hand, both Figures 3 and 4 recorded the lowest COF value of 0.103 against the COF values of 0.117 and 0.143 recorded by Shell Turbo T46 oil and 0 wt.% TBHQ inclusion (without TBHQ).

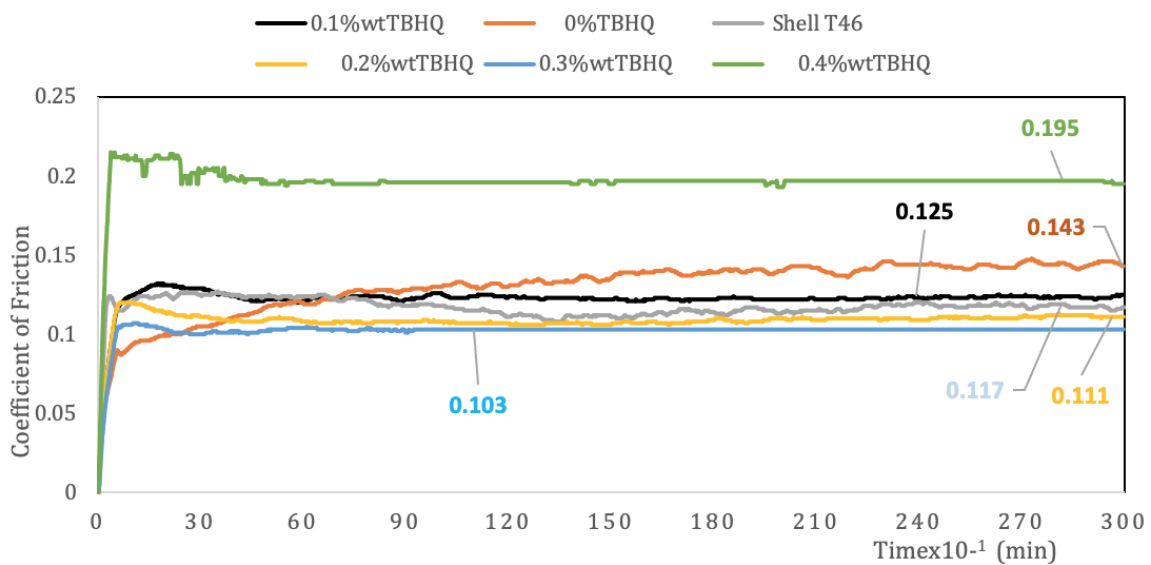


Figure 2: COF of different concentration of TBHQ in PO compared in relation to T46 mineral lubricant.

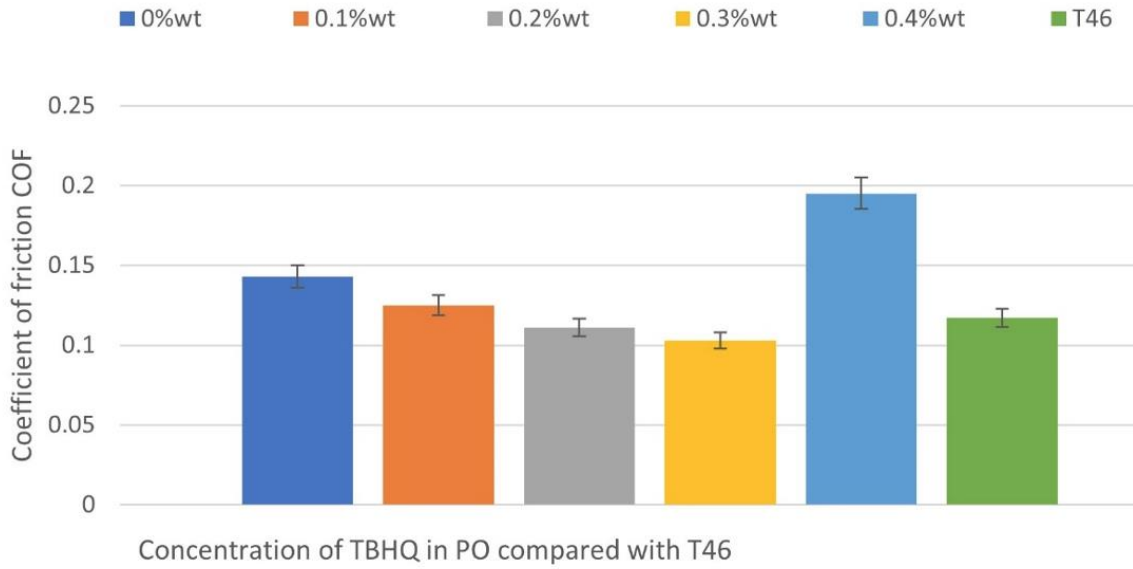


Figure 3: COF of PO + TBHQ concentrations oils compared with shell T46.

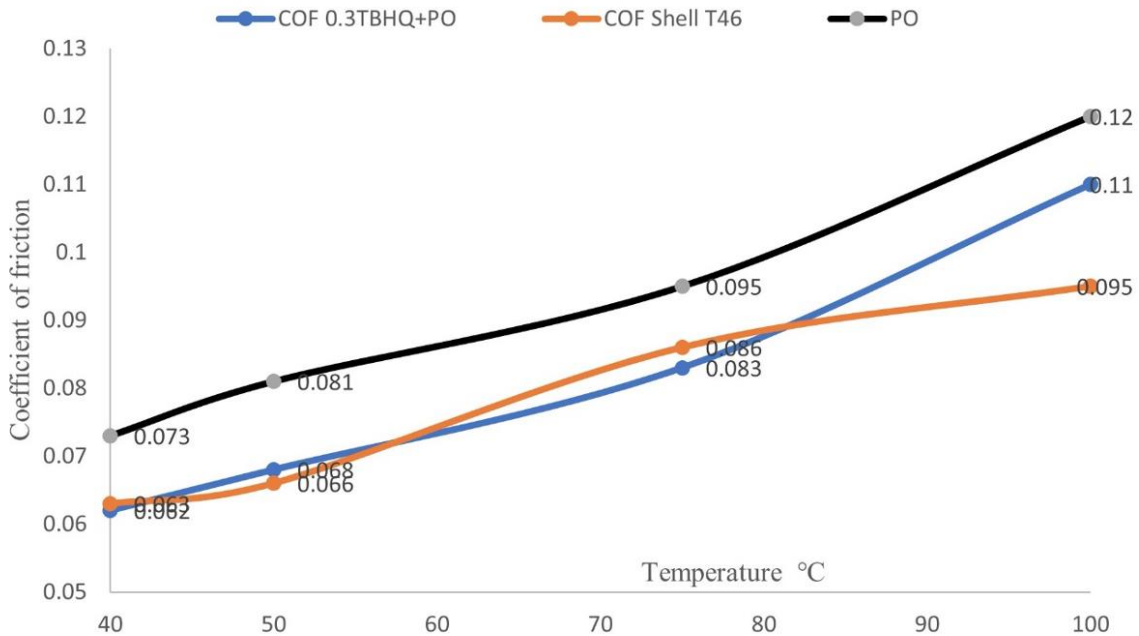


Figure 4: Effect of 0.3 wt% of TBHQ on the Tribological performance of PO at moderate temperatures.

### 3.2 Weight Loss in Aluminum Plate

Aluminum plate ASTM B209 as a soft metal alloy is the softest of the tribo-pairs used in the tribological tests carried out. Rubbing against steel ball of AISI E 52100 with hardness 60-67 HRC (Rockwell) was observed to remove appreciable fragments of aluminum plate during the LRT operation. Since 0.3%wtTBHQ +PO has the most probable concentration to lessen the COF amongst the examined concentrations as shown in Figure 3. It was selected for comparison with PO and T46 as shown in Figure 4. Hence, it showed clearly that there was very close correlation in the average COF value of PO with 0.3 wt.% TBHQ inclusion and that of T46 oils until 80 °C when their COF curves respectively climbed and dipped, possibly due to the difference in their viscosity index VI as shown in Table 2. Beyond that temperature the T46 with higher VI maintained steady COF value than 0.3 wt.% TBHQ+PO which ascended as shown in Figure 4. Between 40 °C and 100 °C, the mass of aluminum material removed due to friction was determined using a standard method for weight attrition ASTM D7473 (Zhu et al., 2019).

Figure 5 depicts the pattern in the WL of PO with inclusion of 0.3%wtTBHQ both under 60N and 80N loads. The wear showed a marked proportionalism to load and temperature until 60 °C. Probably, the malleable property of aluminum might cause a disproportionate wear rate at higher temperature. This is possible because compression without wear of aluminium becomes higher at extreme load, pressure and temperature (Pichumani et al., 2018) (Wannik et al., 2012). Averagely, 50 N was an appropriate medium load considering the weight loss pattern in Figure 5, material WL was apparently proportional to load and temperature until 50 °C for both 60 N and 80 N loads in all the oil samples. Notwithstanding, the performance of 0.3 wt.%TBHQ under the load of 60 N showed remarkable decline in its WL values at 60 °C. Only PO without TBHQ under 60N load showed lowest WL between 40 °C to 70 °C. The implication of this is that the saturated fatty acid chain of the oleic acid in PO which was not agitated by dispersion of the particles of TBHQ, hence the saturated fatty acids remained bonded until a higher pressure due to load or temperature effect weakens their bond, giving room to thinner film thickness in case of PO without TBHQ. It was demonstrated that T46 contributed to reduced WL more significantly at moderately, high temperatures due to its higher VI as shown in Figure 6.

Figure 6 shows the effect of 0.3 wt.% inclusion of TBHQ in PO on the WL of Aluminum at different temperatures. WL at 40 °C and 50 °C portray PO recording the least wear under 60 N load. At 60 °C, PO and 0.3 wt.% TBHQ+PO were shown to record same WL of 0.003g under 60 N but the 80 N load has 0.3 wt.% TBHQ+PO manifesting reduced WL of 0.004 while PO recorded 0.015g WL. Furthermore, at 75 °C, 0.3 wt.% TBHQ only had significant effect on the 80 N load in which WL reduced from 0.008g to 0.005. However, appreciable effect was presented at 100 °C by inclusion of 0.3 wt.% TBHQ in PO both 60 N and 80 N loads. WL reduced from 0.008g to 0.006g in the 80 N load while for 60 N load, WL reduced from 0,008g to 0.005g. Addition of 0.3 wt.% of TBHQ to PO therefore showed significant influence in wear loss WL of aluminium with respect to load and temperature conditions. Table 3 further revealed the significant wear reduction effect of TBHQ at 80N load recording highest performance of 67.7% wear reduction at 50 °C and 25% reduction at 100 °C. This can be further explained by the effect of 0.3 wt.% of TBHQ on the viscosity index of PO as presented in Table 2. It showed that inclusion of TBHQ enhanced the VI of PO by 16.1% from 205 to 238. The implication therefore is that the improvement on the VI could be responsible for the WL reduction at 100 °C under both 60N and 80N loads which indicated moderately extreme conditions.



Table 2: Effect of TBHQ on viscosity index VI of PO lubricant

S/N	Base oil	Density at 25 °C (g/cm <sup>3</sup> )	Kinematic viscosity (cSt)		Viscosity index VI
			40 °C	100 °C	
1	Palm oil PO	0.8388	33.6	7.6	205
2	PO+0.3wt.%TBHQ	0.8460	38.9	9.4	238
3	Shell T46	0.8440	43.8	6.7	106

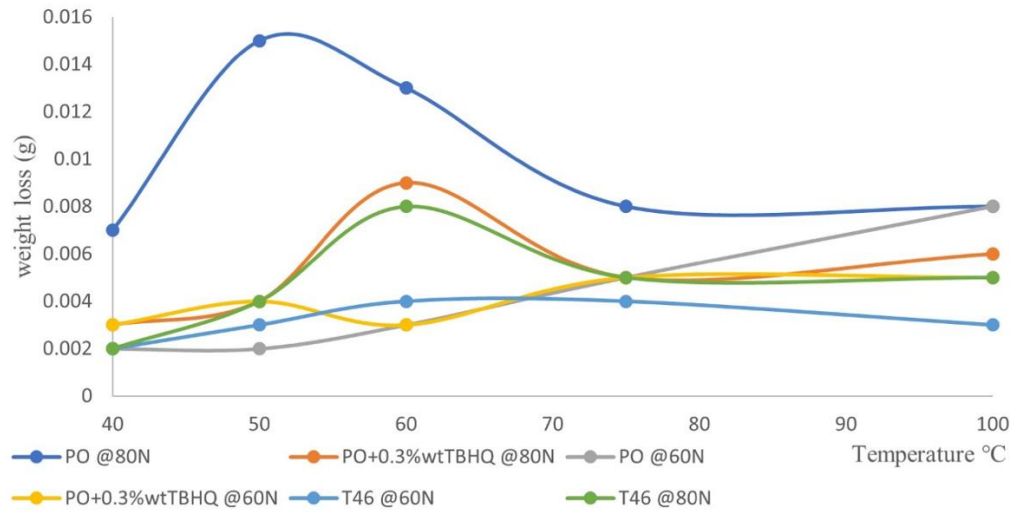


Figure 5: Weight loss in aluminum lubricated with PO oils.

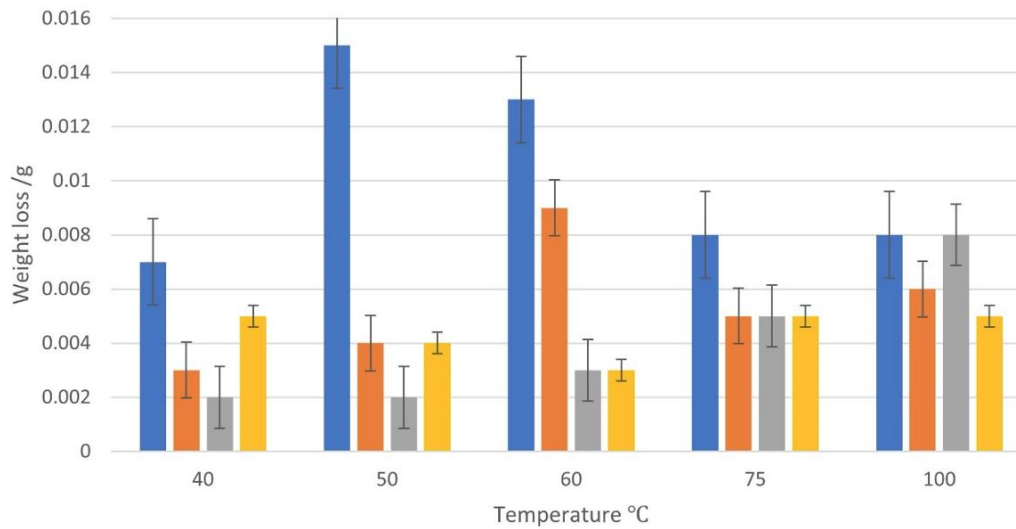


Figure 6: Effect of TBHQ on weight loss in PO at different temperatures under 60N and 80N loads.

Table 3: Aluminium wear (WL) due to TBHQ addition to PO lubricant at different temperatures.

Temp. (°C)	WL of Al (g) under 60 N			WL of Al (g) under 80 N		
	0.3 wt.%	PO	WL	0.3 wt.%	PO	WL reduction
40	0.005	0.002	Nil	0.005	0.007	28.6
50	0.004	0.002	Nil	0.0042	0.013	67.7
60	0.003	0.003	Nil	0.009	0.013	30.8
75	0.005	0.005	Nil	0.0052	0.008	35
100	0.006	0.008	37.5	0.006	0.008	25

### 3.3 Antioxidation

Figure 7 showed the effect of TBHQ on the oxidation. The oxidation onset temperature OOT of PO with TBHQ was recorded as 217.5 °C whereas the OOT of PO without TBHQ inclusion was 178.5 °C. The implication of this is that PO with addition of TBHQ could not commence oxidisation until the temperature was 39 °C higher than that without TBHQ. The implication of this is that the presense of TBHQ in PO was responsible for enhacement of oxidation onset temperation upwards. Thus, TBHQ could enhance the performance of PO and elongate its oxidation stability beyond its ordinary state without the additive.

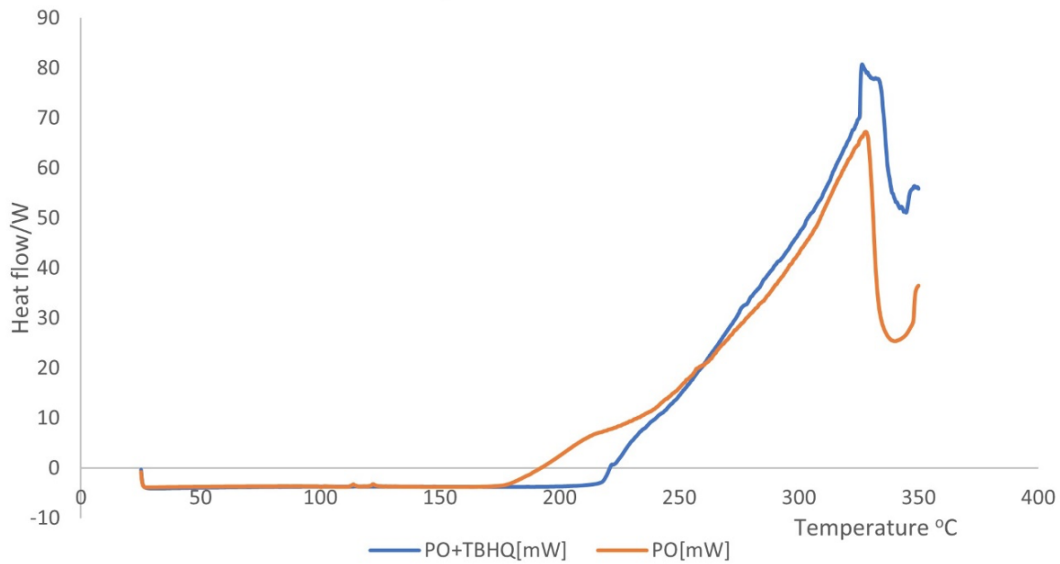


Figure 7: Effect of TBHQ on the Oxidation Onset Temperature OOT of PO lubricant.

### CONCLUSIONS

The study significantly demonstrated the effect of tert-butylhydroquinone on palm oil lubricants under sliding friction conditions using linear reciprocating tribometer. Part of novelty revealed was the concentration of TBHQ indicated for the tribo-pair optimum COF reduction in concentrations examined. Thus, substantiating previous attempts towards presenting palm oil as alternative bio lubricant. It supports previous efforts of researchers and improvements on the

evolving modifications to vegetable oils through nano material addition to consistently enhance the performance of bio lubricants. 0.3%wtTBHQ has shown significant potentials in reducing coefficient of friction in aluminum against steel ball tribo-pairs. Wear loss in aluminum experienced highest reduction of 67% for load of 80 N at 100°C and COF lessened by 17.6% from 0.125 to 0.103 with TBHQ addition to PO. Meanwhile, TBHQ inclusion in PO also enhanced its viscosity index VI from 205 to 238, signifying greater possibility for applications at medium temperature. The demonstration of this significant rise in the viscosity index VI of PO because of 0.3%wt of TBHQ inclusion is another positive contribution of TBHQ to PO for use as lubricant. Results of the Differential scanning calorimetry DSC test showed that the oxidation onset temperature OOT was also prolonged from 178.5 °C to 217.5 °C, i.e., 39 °C signifying 21.8% improvement of its oxidation onset temperature. Thus, palm oil when modified by TBHQ antioxidant can function as a sustainable bio lubricant. Accordingly, it can possibly be further developed to serve as alternative for non-biodegradable mineral oils. Research conducted in this direction will further improve lubrication with the use of biodegradable non-hydrocarbon-based lubricants like palm oil and other potential vegetable oil to secure the ecosystem from hazardous difficult to dispose fossil-based oil lubricants towards abating the menace of environmental degradation.

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