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# PRACTICAL METHODS TO DETERMINE THE THERMAL STABILITY OF MOTOR OILS

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**Abstract**

A performance of motor oil is influenced by base oil types and additives. Many ingredients such as antioxidants, viscosity index improvers, detergents, and antiwear agents are added to lubricants in order to improve its performances. Stability of motor oil is a concerned factor and widely used to measure performance of automotive lubricants. Therefore, understanding the stability of motor oil products is an initial step for improving the quality of lubricants. In this study, practical thermal analysis methods of conventional differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were used to evaluate the stability of 20 commercial motorcycle oils in 5 American Petroleum Institute (API) grades. Oxidation induction time (OIT), oxidation onset temperature (OOT), volatility loss and activation energy were used as stability indicators to determine performances in thermal degradation process at 100°C for 8 weeks. The OIT and OOT were employed to evaluate oxidation stability. It was found that the latest API groups (SJ and SL) were more stable than the previous categories such as SC, SF, and SG. Volatility and apparent activation energies were used to determine thermal stability by TGA instrument. Stability of motor oils had no correlation with the API category. Significant variation of OIT, OOT, volatility and the activation energy within the same API category were observed during thermal degradation.

***Keywords****: thermal stability; degradation; oil oxidation; activation energy of motor oils.*

## 1. Introduction

A lubricant market is driven by the growing automotive industry. Total lubricant demand is estimated to be 2.5 billion liters per year in 2015 and projects to reach 3.2 billion liters per year in 2020 [1]. In addition, motorcycles have always been a dominant market. A number of motorcycles on the roads have been growing by approximately 18 million units per year. The high demand for lubricant products in developing countries come with several problems such as counterfeit lubricants, reusing lube oil without appropriate re-refining processes and mixing lubricants with poor quality oils. Using these low quality lubricants not only impacts engine performances but also generates hazardous chemical vapors to the environment. These chemicals contribute to chronic hazards including mutagenicity and carcinogenicity, which are very toxic to humans [2]. Oxidation stability and volatility are important factors to be considered as indicators on the quality and performance of lubricants. Poor quality motor oils express a high level of volatility and low oxidation stability. These properties directly affect the physical and chemical properties of lubricants, for example, volatility relates to the fire and flash point of the lubricating fluid in high-temperature conditions [3]. Oxidation property of a lubricant can lead to several undesirable results, such as increased oil viscosity, the formation of corrosive acids, and sludge buildups, which accelerating engine corrosion [4].

Thermal stability determination of lubricant by thermal analysis techniques are important for the modern engine lubricants. Pressurized differential scanning calorimetry (PDSC) instrument is used to determine the oxidative stability of engine oils such as OIT and OOT under isothermal and dynamic conditions [5-8]. This technique offers fast analysis (within an hour), high sensitivity, less waste sample after testing and reproducibility of measurements [9]. However, the PDSC instrument is not as common as the conventional DSC. In general thermal analysis laboratories, the conventional TGA and DSC are widely used for numerous applications for a variety of materials. Many studies have reported that the conventional DSC could be used as a tool to classify and evaluate the effectiveness of oxidative inhibitors, which added to hydrocarbon products [10-12]. In addition, the evaporation loss of lubricating oil is also important in engine oil lubrication. It contributes to oil consumption in an engine and can lead to a change in the properties of the oil, which could produce air pollution [13]. Therefore, volatility of lubricant is an important factor that impacts the performances of formulated engine oil. TGA technique is a common method for investigating weight loss of a sample while the temperature is changed over time [14]. The ASTM D 6375 standard test method is used for determining evaporation loss of lubricating oils by the thermogravimetric analyzer. Specifically, Noack method gives useful volatility information in order to evaluate the volatility properties of motor oils [15]. Following this standard, a lubricant sample is quickly heated to 249°C in the dynamic section then held isothermally. A TGA curve provides a percent mass loss versus time, as shown in Fig. 1. For evaluation of oxidative stability by using the conventional DSC instrument, the oxidation induction time (OIT) and oxidation onset temperature (OOT) can be used to assess oil stability [16]. A typical OIT measurement is a plot of heat flow (mw/mg) versus time (min). The OIT technique indicates the time from the beginning that oil is exposed to oxygen gas in the isothermal condition until onset temperature peak occurs as shown in Fig. 2.

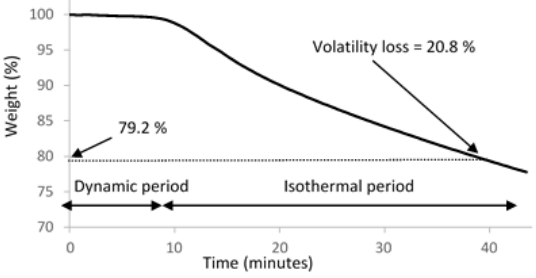

Fig. 1. Thermogravimetric analysis determination of the evaporation loss (Noack volatility)

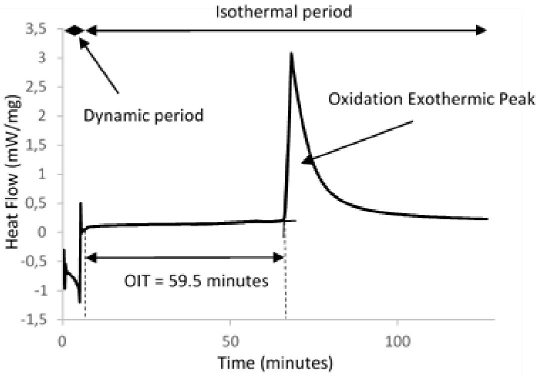

Fig. 2. Differential scanning calorimetry curve for the oxidation induction time (OIT) determination

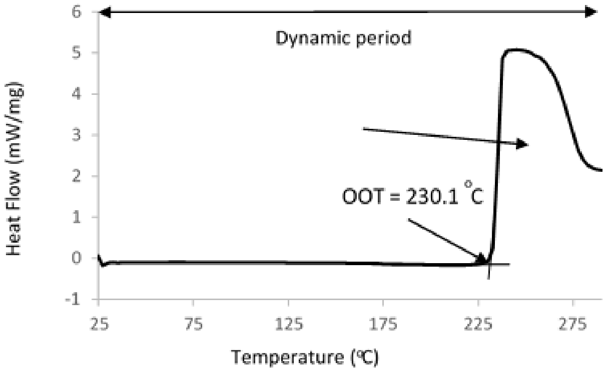

Fig. 3. Differential scanning calorimetry curve for the oxidation onset temperature (OOT) determination

This test method is standardized by the ASTM E 1858 standard [17]. The OOT is also using to evaluate the oxidative stability of lubricant. This method measures the oxidation onset temperature, which is standardized by the ASTM E 2009. In the beginning, a sample is heated with a constant heating rate. Simultaneously, one atmosphere of oxygen is filled in until the exothermic peak emerges. The OOT value is defined as the temperature at the onset of the exothermic oxidation peak [18] as shown in Fig. 3.

Moreover, activation energy is another indicator utilizing kinetic analysis to determine the stability of lubricant. This application of TGA is based on the iso-conversional method of kinetic analysis under non-isothermal conditions, which is frequently used to determine the activation energy of oxidative degradation study in oils [19-20]. It can be used as an analytical device for accurately measuring weight change of a material subjected to a temperature history. The weight loss information is used to determine the activation energy of lubricant samples. The high quality motor oil depends on the type of base oil as well as additives [21]. It should have good stability and volatility properties because these factors lead to serious damages to the engine. Determination of performances in an automotive lubricant through conventional thermal analysis techniques are beneficial for the formulation of lubricant before a full-scale engine testing, which is expensive and takes a longtime. Therefore, these practical methods can be utilized for improving the thermal performance of base oils and additives. In addition, thermal stability information should be provided to customers, they could identify performances of lubricants and select high performance lubricant without any influences of false commercials.

In this work, we have investigated the thermal stability of 20 motorcycle oils during thermal degradation for 8 weeks by using practical thermal analysis methods to obtain values of OOT, OIT, volatility loss and activation energy. The change of quality in lubricants were estimated by a correlation of a trend in thermal stability.

## 2. Materials and methods

### 2.1. Motor oils

Twenty conventional motorcycle oils were obtained from 20 brands commonly available in local lubricant markets. The tested lubricants consisted of international brands and local brands, which were suitable for 4-stroke motorcycle engines. In this investigation, viscosity grade of all samples were Society of Automotive Engineers (SAE) 40 of which 5 brands in SC category; 5 in SF; 4 in SG; 3 in SJ and 3 in SL category. About 30 mL of each lubricant fluid was filled in a glass cylinder container (2.5 cm diameter and 9.5 cm height) without closing a lid and stored at 100°C for 8 weeks. Every 2 weeks, 2 mL of each sample was collected for determination of volatility loss, OIT and OOT in order to observe changes of performances.

### 2.2. Oxidation onset temperature (OOT) analysis according to the ASTM E 2009

According to the ASTM E 2009 standard for the OOT test, approximately 3 mg of lubricant samples were heated at a constant rate of 10°C/min from 25°C to 100°C in an oxygen atmosphere with constant flow rate of 50 mL/min. The oxidation onset temperature was specified from its DSC curves of the exothermic process.

### 2.3. Oxidation induction time (OIT) analysis according to the ASTM E 1858

Thermal stability of lubricants was analyzed in term of OIT test according to the ASTM E 1858 standard. Approximately 3 mg of sample was placed into an uncovered aluminum pan and were held initially at 25°C under nitrogen flow of 50 mL/min. The temperature was increased to 210°C with a heating rate of 40°C/min, still under the same nitrogen flow. When reaching the defined temperature, hold for 5 min and switched nitrogen to oxygen gas at 50 mL/min then held at 210°C (isothermal) for 60 min. The OIT was measured by DSC signal when an exothermic reaction onset was observed.

### 2.4. Volatility analysis according to the ASTM D 6375

The procedure followed the ASTM D 6375, using 61 ± 3 mg of lubricant samples in an opened aluminum crucible with an internal diameter of 0.56 cm. The temperature was increased from 50°C to 220°C with a heating rate of 100°C/min and followed by heating to 249°C at 10°C/min. The isothermal period was held at 249°C for 30 min with air purge at a total flow rate of 80 mL/min. The percentage of evaporation loss of lubricants was determined by the TGA curve of the sample at 30 min after isothermal period. The TGA results were used to compare the volatility of samples for performance evaluation.

### 2.5. Determination of activation energy

The conventional TGA was used to evaluate the kinetics of motor oils. Non-isothermal thermogravimetry has been applied to determine activation energy. Approximately 5.0 mg of selected sample was filled in a 70 µL alumina crucible and placed into TGA instrument. Samples were heated from the ambient temperature to 600°C under a nitrogen atmosphere with a flow rate of 100 mL/min. The experiments were conducted at 4 constant heating rates of 5, 10, 20 and 30°C/min as shown in Fig. 4 at percent conversion of 10, 20, 30, 40, 50, 60, 70, 80 and 90% were utilized to determine the activation energy. The decomposition of oil samples was evaluated to quantify the rate of aging of oils at different conditions. The kinetic models are based on the following fundamental rate equations [22].

$$\frac{d\alpha}{dt} = Aexp\left(-\frac{E}{RT}\right) f(\alpha) \qquad (1)$$

where $E$ is the activation energy of the kinetic process; $A$ is the Arrhenius parameter also called the pre-exponential factor and $R$ the universal gas constant. The conversion dependent function, $f(\alpha)$ is assumed that the degradation reaction is a simple $n$th-order reaction.

The conversion dependent term can be expressed as

$$f(\alpha) = (1-\alpha)^n \qquad (2)$$

where $n$ is the order of the kinetics, which is characterized by the first order kinetics $n = 1$ for decomposition of oil [23].

The integral form of the equation (1) can be written as:

$$g(x) = \int_0^x \frac{dx}{f(x)} = \frac{A}{\beta}\int_{T_0}^{T} exp\left(-\frac{E}{RT}\right) dT = \frac{AE}{\beta R} p\left(\frac{E}{RT}\right) \qquad (3)$$

where $\beta$ denotes the heating rate of ethe xperiment.

Kissinger-Akahira-Sunose (KAS) method is based on the Coats, and Redfern approximation [24], which has been employed and the function of the integral isoconventional KAS method is given by [25].

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{Eg(x)}\right) - \frac{E}{RT} \qquad (4)$$

Equation (3), temperatures at various chosen values of conversions are determined at different heating rates. The activation energy can be obtained from the slope of the strength-line by plotting $\ln(\beta/T^2)$ on y-the axis versus $1/T$ on x-the axis at a given level of the conversion as shown in Fig. 5.

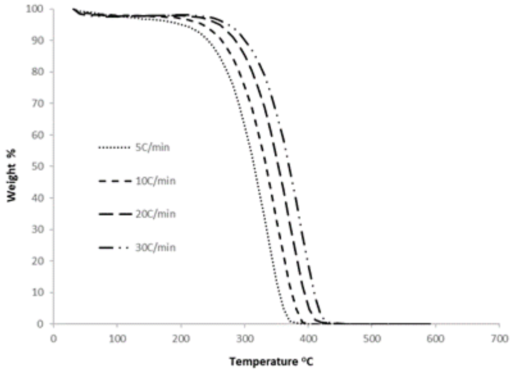

Fig 4. Typical TGA curves for weight loss profiles at different heating rates of SC1

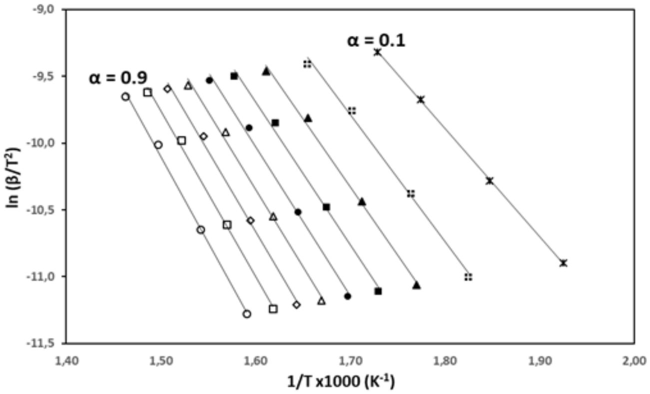

Fig 5. The Kissinger-Akahira-Sunose (KAS) plots for thermal degradation of lubricant at different rates and conversion level (α) : 0.1-0.9

## 3. Results and discussion

### 3.1. Initial product performances

Twenty commercial motor oils having the same SAE viscosity grade at number 40 were investigated to determine the oxidative stability and volatility before thermal degradation test. They were in 5 categories including SC, SF, SG, SJ, and SL. These engine oil samples were analyzed according to the three ASTM standards and the results of volatility loss, OIT and OOT are shown in Table 1.

Table 1. The initial volatility loss (%), oxidation onset temperature (OOT, °C) and oxidation induction time (OIT, min) of twenty lubricants having the following API: SC, SF, SG, SJ, and SL categories

| Lubricants API | Volatility loss (%) | OIT (min) | OOT (°C) | Lubricants | Volatility loss (%) | OIT (min) | OOT (°C) |
|---|---|---|---|---|---|---|---|
| SC01 | 8.3 | 9.4 | 246.2 | SG01 | 19.0 | 15.0 | 248.0 |
| SC02 | 4.7 | 7.7 | 235.1 | SG02 | 17.8 | 55.1 | 266.4 |
| SC03 | 4.8 | 8.3 | 236.7 | SG03 | 14.1 | 59.8 | 276.5 |
| SC04 | 6.8 | 5.2 | 228.1 | SG04 | 11.5 | 48.7 | 263.9 |
| SC05 | 5.6 | 8.3 | 230.4 | SJ01 | 10.2 | 58.0 | 272.0 |
| SF01 | 15.0 | 23.4 | 257.0 | SJ02 | 11.8 | 66.2 | 282.7 |
| SF02 | 11.8 | 16.0 | 248.5 | SJ03 | 20.8 | 57.9 | 271.3 |
| SF03 | 8.5 | 17.9 | 249.7 | SL01 | 21.2 | 65.0 | 279.0 |
| SF04 | 8.0 | 8.7 | 238.8 | SL02 | 13.5 | 115.0 | 293.9 |
| SF05 | 6.3 | 17.1 | 250.2 | SL03 | 6.6 | 92.7 | 287.8 |

Stable motor oil should have high oxidation temperature (OOT) and long oxidation time (OIT) value. The results revealed that the average of OOT value for each API category increased from 235°C to 287°C and got better in the alphabetical order of the oil categories. There was a gap between the minimum and maximum of OOT values within each category. The range for SC, SF, SG, SJ, and SL were 18.1, 18.2, 28.5, 11.4 and 14.9, respectively, and these ranges reflected the quality of motor oils within the group. A narrow range implied that members of the same API had almost the same quality while there was quite a different oxidative stability in the group with a large range. The relationship of the API categories and the oxidative stability evaluated by OOT also showed that the lubricants in the latest API service category (SL) was more stable than the previous category oils (SC, SF, SG, and SJ). The mean of the OOT was in the following order from the lowest to the highest: SC (235.3°C), SF (248.8°C), SG (263.7°C), SJ (275.3°C) and SL (286.9°C). The OOT value was a suitable tool to identify a poor oxidative oil in a category. For example, in SF category, SF04 had the lowest OOT of approximately 239°C, which was significantly lower than the OOT mean of 248.8°C. Therefore, the OOT values could be used as an indicator to evaluate the thermal stability of motor oils. The stability of the 5 API categories was also determined by OIT showing that the OIT of lubricants in each API category was in good agreement with the OOT data. Increasing the OIT accompanied with a higher oxidation temperature. Note that the two motor oils (SC3 and SC5) in SC group had a similar OIT value (8.3 mins), but the results of OOT were different: 230.4°C and 236.7°C, respectively. For the most stable oil, SL02 had the longest OIT (115 mins) while OOT was the highest value (293.3°C) among all investigated motor oils. The volatility property provided by the Noack volatility test of the 20 lubricant fluids are shown in Table 1. There were 6 oils including SF01, SG01, SG02, SG03, SJ03 and SL01 whose evaporative loss were more than 14%, especially, SJ03 and SL01 had more than 20% of volatilization while SC2 and SC3 were good volatility oils having the lowest volatility. Therefore, the volatility rate is also an important factor for lubricants. A high volatile oil should be considered when using these oils.

In this study, there was no significant correlation between volatility loss and the API category. For this set of commercial lubricants, it was found that there was also no direct relationship between SAE viscosity grade and volatility because all samples were in the same SAE viscosity grade, but they had different volatility properties. Moreover, the SAE viscosity grade was not a good indicator for providing the volatility information to the customers. The API category was also not a good indicator to determine the volatility of each motor oil, and there was no volatility trend when API category change from SC to SL. However, there was a good correlation between the API category and oxidative stability that the later API category such as SJ and SL was more stable than the previous categories (SC, SF, and SG).

## 3.2. Thermal stability during degradation

Twenty motor oils were degraded at 100°C for 8 weeks, and samples were collected every 2 weeks during the degradation test period. The oxidative stability and volatility results were obtained using DSC and TGA instruments.

Stability of motor oils during thermal degradation were determined in terms of OIT (mins), OOT (°C) and volatility (%) over 8 weeks of aging test at 100°C. The data of 5 lubricants in the API SC category was taken every 2 weeks and plotted as shown in Fig. 6 (a) for OOT (°C) using the left axis, and for OIT (mins) using the right axis. Fig. 6 (b) was volatility of the 5 lubricants in SC grade. The OOT values of the 5 motor oils showed that SC5 was quite a high oxidative stability motor oil to fight against an oxidation because its OOT values of 230°C remained almost unchanged during 8 weeks.

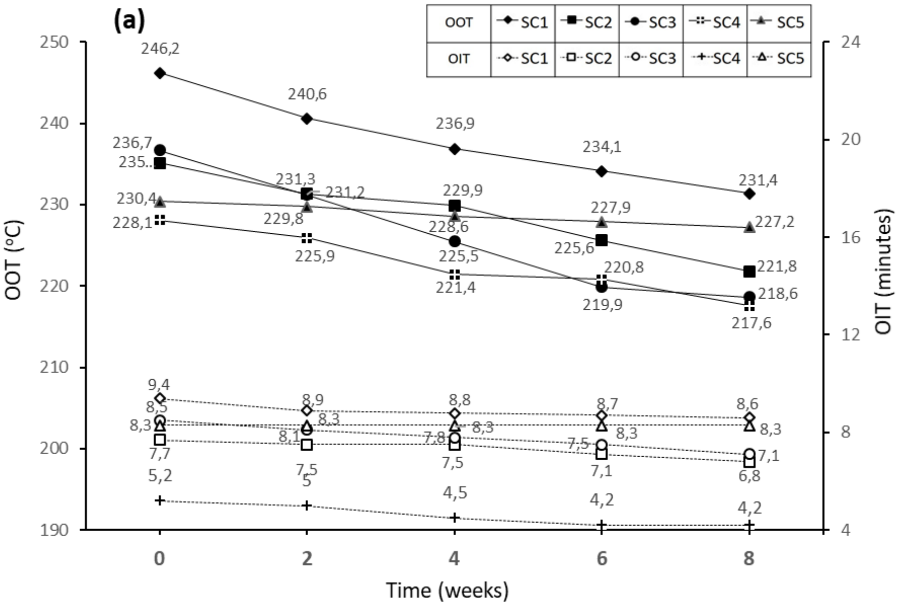

Fig. 6 (a) Values of OOT (°C) shown on the left axis for the upper group of data and OIT (min) shown on the right axis for the lower group of the five lubricants within the API SC grade tested over eight weeks of heating at 100°C

In contrast, OOT of SC1, SC2, SC3 and SC4 degraded over the testing period. Specifically, SC1 showed the highest OOT but degraded from 246.2°C to 231.4°C after 8 weeks. For SC2, SC3, SC4 and SC5, OOT results revealed that before degradation test (0 week), SC3 had higher OOT than SC2, SC4 and SC5. However, 8 weeks later, SC5 was more stable than SC2, SC3, SC4 and SC2 was more stable than SC3 and SC4, which had the lowest OOT of 217-218°C. For oxidative stability determined by time of oxidation at isothermal methods, so called OIT values, the 5 motor oils had similar oxidative stability trend. Their OIT values slightly decreased over the period, except SC5, which remained unchanged at 8.3 mins. SC1 had the highest OIT values (9.4 mins) over 8 weeks which only slightly decreased by 0.8 mins at the end of the test. For SC2 at the beginning of the test, it had lower OIT than SC3. However, after 8 weeks their OIT values were almost the same at approximately 7 mins. The lowest stability in SC group was SC4. It had the shortest OIT value at every oxidation point. These OIT values were significantly lower than the others.

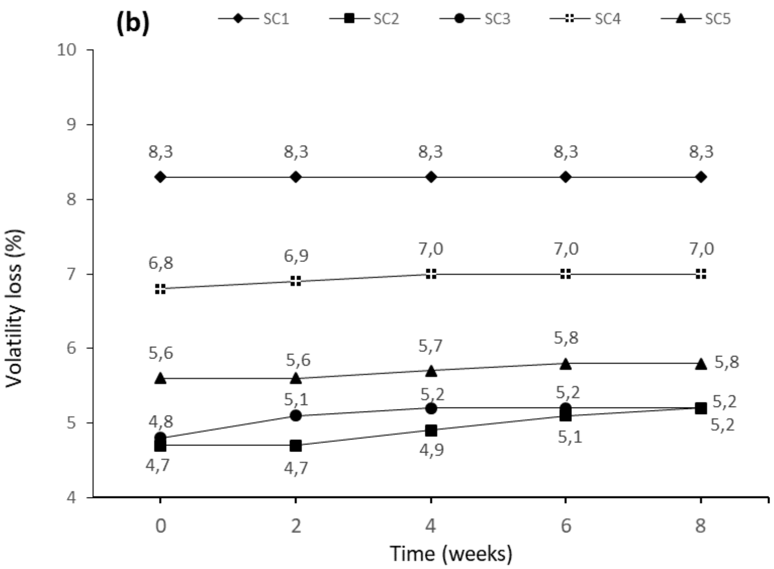

Fig. 6 (b) Volatility loss (%) of the five lubricants within the API SC grade tested after eight weeks of heating at 100°C

Fig.6 (b) showed volatility loss (%) of 5 motor oils in SC grades. Over 8 weeks of thermal degradation at 100°C, the volatility loss changed only slightly from no loss for SC1 to maximum of 0.4% for SC2. It was noted that these motor oils did not volatile much in 8 weeks. Moreover, volatility loss revealed that SC2 and SC3 had almost the same volatility loss of stock condition at two weeks. SC3 increased volatility loss but SC2 still unchanged. After two weeks, SC3 volatility remained steady while SC2 volatility slowly increased. Both SC2 and SC3 had similar volatility loss of 5.2% at the end of the degradation period. From the data shown in Fig. 6 (a and b) it could be concluded that SC5 was a good stable motor oil. It had quite high oxidative stability and volatility although it did not have the best OIT, OOT and volatility properties. In contrast, SC1 showed the best oxidative stabilities in term of OOT and OIT but its evaporation was very high. Therefore, SC1 was not a good motor oil in this group.

The oxidative stability test for 8 weeks at 100°C for SF group were shown in Fig 7 (a). The trend of OOT for the SF 5 motor oils decreased over the testing period. SF1 had the highest OOT values throughout 8 weeks while SF4 had the lowest OOT value. For SF2, SF3, and SF5, they had almost the same OOT value in the fresh condition. After two weeks, the OOT of SF3 was higher than that of SF5 and SF2; all three motor oils declined slowly to an almost similar value (234-235°C) at the end of the degradation test. In SF group, OIT of all 5 samples decreased within 8 weeks. SF1 was the most stable motor oil, and its OIT values were the highest during the degradation period. In contrast, SF4 had very low stability when compared with the others although its OIT was almost unchanged. Moreover, the OIT results reveal that the oxidation property trends of SF2, SF3, and SF5 went down over the period. After 4 weeks, SF2 expressed quite high stability because its OIT remained unchanged and it was higher than that of SF3 and SF5. However, the OIT decreased after that, and it was the same as SF3 at the end of the testing while SF5 had higher OIT than SF2 and SF3.

Volatility loss (%) of all oils was shown in Fig 7 (b). There were 4 motor oils including SF1, SF2, SF3, and SF5 that did not change their volatility property while SF4 increased its volatility loss by 0.8% during 6 weeks and stayed constant at 8.8% until the end of the degradation test. The volatility property of all aged oil samples after 8 weeks showed that SF3 and SF4 had almost similar volatility loss of approximately 9% while SF1 and SF2 had high volatility approximately 15% and 12%, respectively. By comparison, SF5 was the best oil in term of volatilization in this group because of the lowest volatility loss of about 6%. According to the oxidation property and volatility loss, it was obvious that SF2, SF3, and SF5 had good oxidative stability. However, when considered volatility property, SF5 had the best oxidation and volatility property. In contrast, SF1 was the best in terms of oxidative stability but poor volatility. A high performance lubricant requires high oxidative stability and low volatility rating.

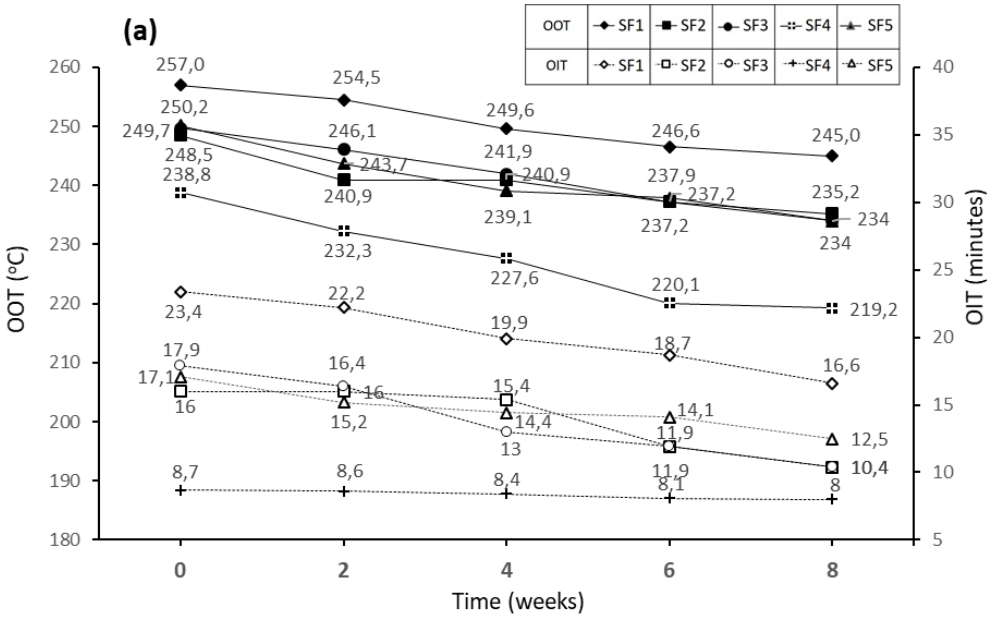

Fig. 7 (a) Values of OOT (°C) shown on the left axis for the upper group of data and OIT (min) shown on the right axis for the lower group of the five lubricants within the API SF grade tested over eight weeks of heating at 100°C

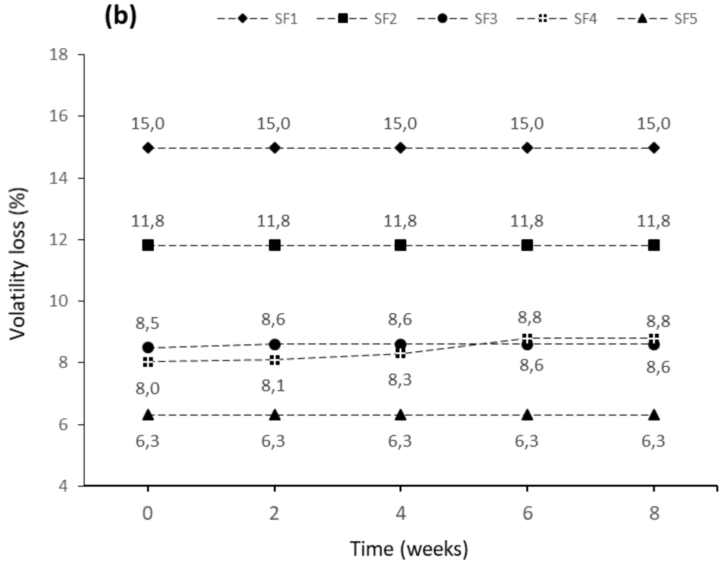

Fig. 7 (b) Volatility loss (%) of the five lubricants within the API SF grade tested after eight weeks of heating at 100°C

Differences of the thermal stability of four motor oils in the SG group was determined by dynamic OOT (°C) and isothermal OIT (min) and were shown in Fig. 8 (a). The oxidative stability property in terms of OOT showed that SG3 had the highest OOT and stayed relatively constant during the degradation test. This behavior indicated that SG3 had good oxidative stability compared with the rest. SG2 performed slightly better than SG4 within 6 weeks. After that, the OOT oxidative stability of both oils was nearly the same at approximately 259°C. SG1 had the lowest OOT over the degradation test. At the end of the degradation test, OOT of SG1 decreased by 12.5°C while the other lubricants such as SG2 SG3 and SG4 had smaller changes of 7.4, 5.7 and 5.4, respectively. For this reason, it was concluded that SG1 had the lowest oxidative stability in SG group. OIT test of four SG motor oils revealed that throughout the degradation test, SG2 and SG3 were the most stable oils for SG group.

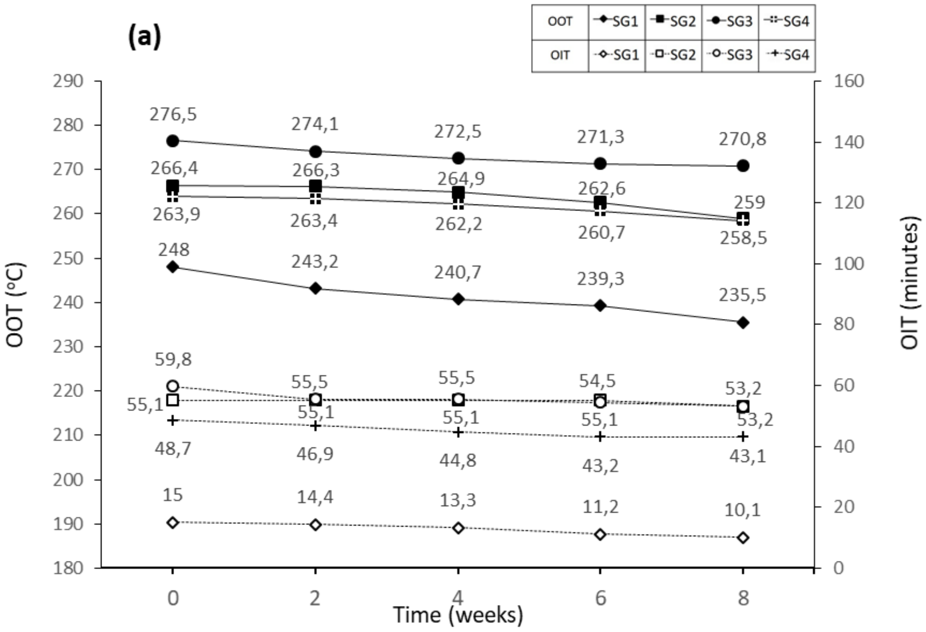

Fig. 8 (a) Values of OOT (°C) on the left axis (the upper group) and OIT (min) on the right axis (the lower group) of the five lubricants within the API SG grade tested over eight weeks of heating at 100°C

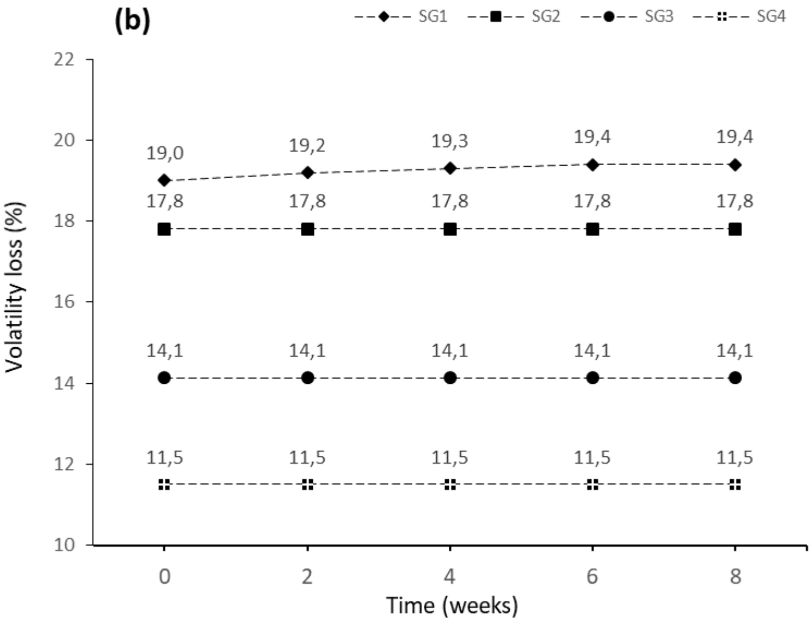

Fig. 8 (b) Thermal degradation test in eight weeks in terms of volatility loss (%) of the five lubricants within the API SG grade tested after eight weeks of heating at 100°C

The OIT results of both oils were the same after 2 weeks. At the end of the degradation test, SG2 and SG3 had OIT at 53.2 mins, which was the highest oxidation time in this SG group. SG4 was more stable than SG1 but its oxidation time was not as good as that of SG2 and SG3. Therefore, SG1 was the least stable when considered OIT and OOT values.

Fig. 8 (b) showed volatility loss (%) by TGA of four motor oils in SG group. The overall volatility trends of SG2, SG3, and SG4 stayed relatively constant at 17.8, 14.1 and 11.5%, respectively. Only SG1 oil had a different volatility behavior. It was the highest volatile oil in SG category and at the end of degradation, the volatility increased by 0.4%. The results from Fig. 8 (a and b) showed that SG3 was the most dominant in the oxidation properties. It had the highest OOT and OIT during the degradation test. However, SG3 evaporated more than SG4 by 2.6%. This small difference was not significant. Therefore, SG3 had the best performance in SG group.

The results for SJ group were illustrated in Fig. 9 (a). The oxidative stability of three motor oils showed that OOT of all motor oils were reduced with increasing incubation time. SJ2 was more stable than SJ1 and SJ3. Before the degradation process, SJ2 was oxidized at approximately 283°C. After 8 weeks, the oxidative stability decreased by approximately 8°C. The OIT result revealed that stability of SJ1 was higher than SJ3. These 2 oils had almost the same oxidation temperature before the degradation test. Over the period, they had similar oxidation trends. However, SJ1 had better stability than SJ3 because its OOT value was higher. At the end of the degradation process, SJ1 OOT was reduced by only 6.4°C while SJ3 OOT was reduced by 10°C. The OIT results showed the same oxidation trend as the OOT results. SJ2 was the most stable oil in this group because its OIT was the longest while SJ1 and SJ3 had almost the same oxidation induction time. Fig. 9 (b) presented the difference of volatility property (%) over 8 weeks of three oils in SJ category. SJ1 maintained low volatility property and stayed constant in volatility loss over the degradation test. This volatile behavior indicated that SJ1was a good quality motor oil. For volatility loss of the others, there was a small change of 0.1% volatility for SJ2 while SJ3 had the highest volatility loss of 21%. The order of volatilization of 3 oils was SJ3 > SJ2 > SJ1. The thermal stability of SJ group shown in Fig. 9 (a and b) indicated that SJ2 had a better performance in the oxidative stability and volatility than the others.

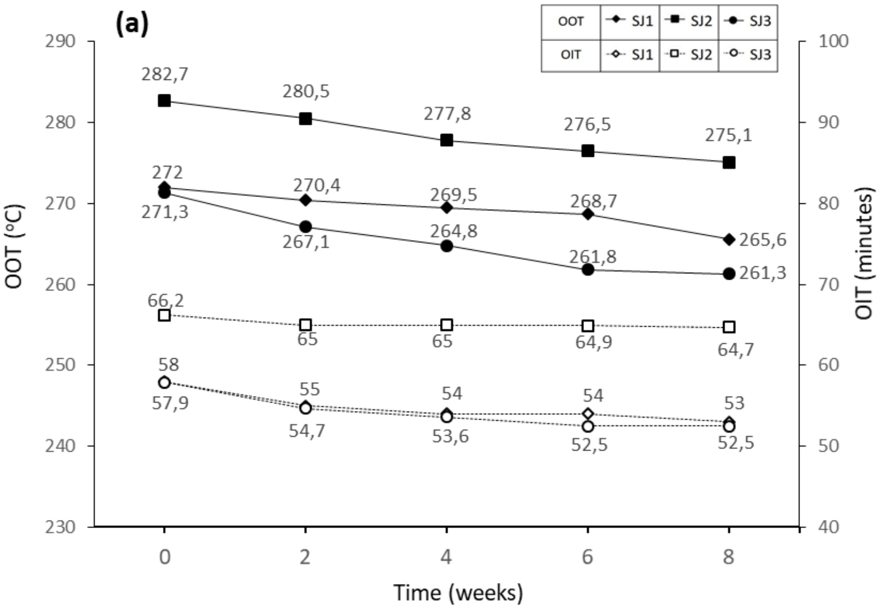

Fig. 9 (a) Values of OOT (°C) on the left axis (the upper group) and OIT (min) on the right axis (the lower group) of the five lubricants within the API SJ grade tested over eight weeks of heating at 100°C

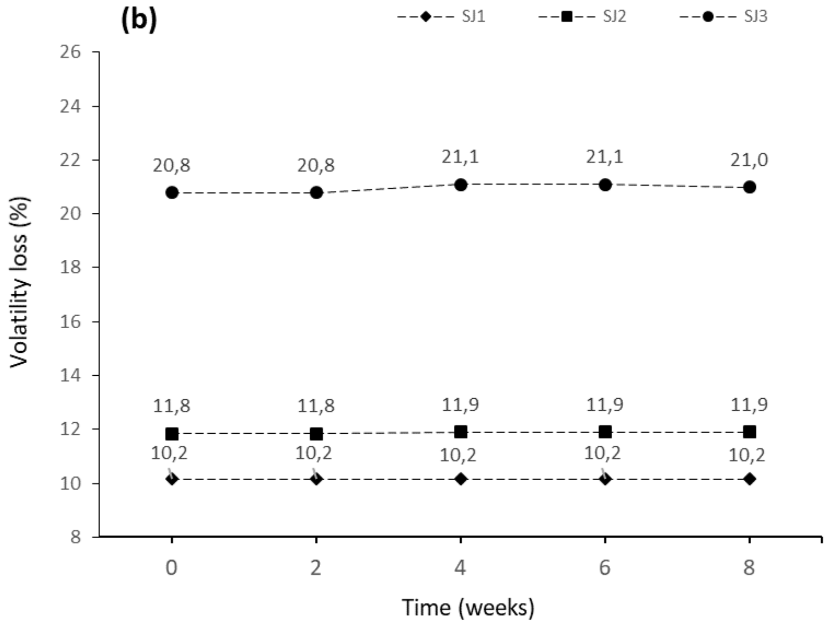

Fig. 9 (b) Thermal degradation test in eight weeks in terms of volatility loss (%) of the five lubricants within the API SJ grade tested after eight weeks of heating at 100°C

The oxidative stability properties of motor oils in SL category were shown in Fig 10 (a). All OOT values were reduced after the thermal degradation process. It was noted that SL2 had the highest OOT before the aging test then reduced by 12.5°C after 8 weeks. The OOT of SL1 and SL3 were lower at 287.8°C and 279°C and decreased by 6.2 and 7.1°C at the end of the degradation test. Although SL2 had the highest oxidative stability that reached 294°C, after 8 weeks the OOT decreased sharply to 281.4°C, which was almost the same temperature as that of SL3. For this reason, SL3 should be identified as a high performance motor oil in SL group. The OIT result showed the oxidation time of SL motor oils in Fig 10 (a).

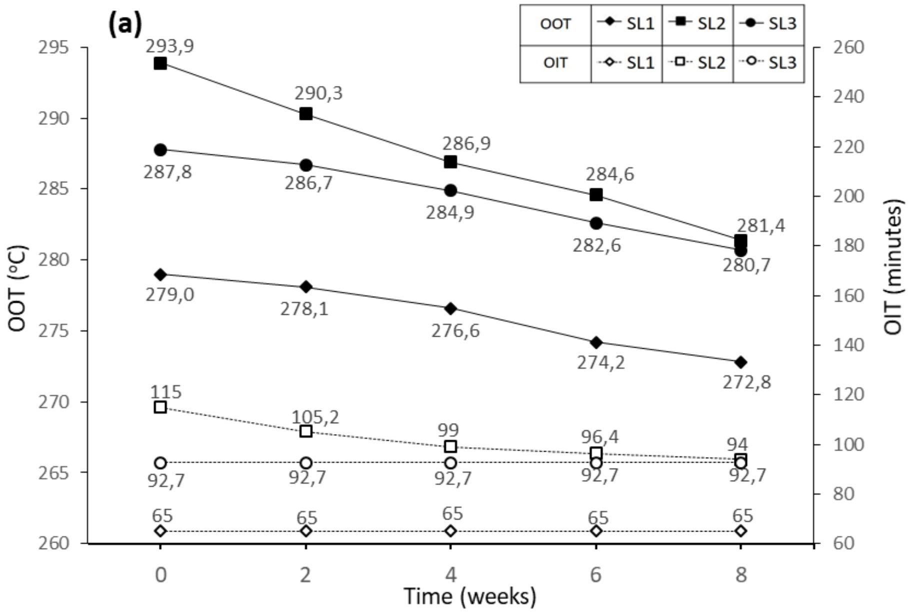

Fig. 10 (a) Values of OOT (°C) on the left axis (the upper group) and OIT (min) on the right axis (the lower group) of the five lubricants within the API SL grade tested over eight weeks of heating at 100°C

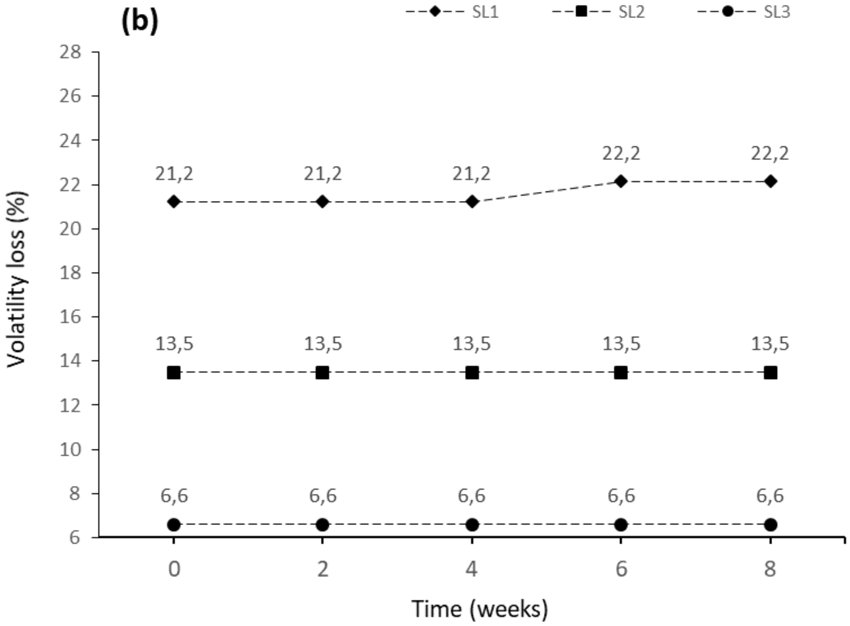

Fig. 10 (b) Thermal degradation test in eight weeks in terms of volatility loss (%) of the five lubricants within the API SL grade tested after eight weeks of heating at 100°C

It could be observed that SL2 oil had the same trend as its OOT results, its OIT reduced by 21 mins over 8 weeks. For SL1 and SL3, OIT results had no change in oxidation time at 65 and 93 mins, respectively. A good stable oil should have constant OIT value and take a long time to be oxidized. The OIT results showed that SL3 was the most stable oil in this group. The volatilization of three motor oils was evaluated and showed in Fig. 10 (b). SL1 had the highest volatility at 21.2% and increased slightly to 22.2% at the end of the test. However, SL3 had better volatility than SL2. The volatility property of SL2 was 13.5% while SL3 was 6.6%. The volatility loss of both oils remained constant over 8 weeks. The results indicated that SL3 had the best volatile property (lowest loss) and remained unchanged. SL3 also had the best oxidative stability in SL group.

The OOT and OIT results were provided by the conventional DSC, which was very useful tool for characterizing the oxidative stability of commercial motor oils. An exothermic peak from DSC output signal expressed the hydrocarbon chains that were oxidized by a free radical mechanism [26]. It expressed level of resistance of a motor oil to oxidation reaction during the testing period [27]. In the analysis of OOT and OIT results, it was observed that there was a good correlation between the latest service API category and oxidative stability. The newer API category showed higher oxidative stability than the old category. This was a clear indication of the latest API standard accompanies with better anti-oxidation properties of the lubricants [28]. The rate of oxidation of lubricant was influenced by the quality and type of base oil as well as the antioxidant additives. Antioxidants played an important role to protect the lubricant in service by limiting the chemical changes and degradation [29]. Moreover, OOT and OIT applications were widely used for assessing the improvement of oxidative stability of lubricants [30-32]. Both OOT and OIT are good for quality identification and should be provided to customers. TGA Noack application was a good method for evaluating the volatility of lubricant. It was useful for estimation of volatility oil at high temperature condition such as engine operating temperature. Rate of volatility depended on the differences in molecular structure of base oil and additives [33]. The results of TGA Noack indicated that increase of volatility in oil was not influenced by the SAE viscosity grades and the API service categories. The differences of volatility in individual motor oil exhibited the lubricant's tendency to vaporize. The high volatility motor oil was not recommended because there may not have enough lubricant to lubricate and reduced the heat generated between surfaces in the engine. Moreover, high volatility lubricants had a chance to be consumed more than low volatility oil at the normal operating temperature of the engine. It caused several serious problems of engines such as oil starvation, which would generate friction, wear and raise temperature of engines [34]. As shown in this study, volatility testing data should be added to product labels in order to better inform customers of the critical information of motor oils. The results of the oxidative stability and volatility during the thermal degradation process revealed useful information about performance of several API grades.

### 3.3. Kinetics of thermal decomposition

Kinetics of thermal decomposition in motor oils were determined using data obtained from TGA result. The temperature ranges were shifted to higher temperatures when heating rate was increased. In addition. Following the KAS method plotted of 1/T versus ln $(\beta/T^2)$ at 9 conversion levels ($\alpha$) at 0.1-0.9, all plots had a strong linear relationship ($r^2 > 0.98$). The apparent activation energies ($E_a$) were calculated from the slope of the linear regression equation at different conversion levels. Table 2-6 are lists of the apparent activation energies of fresh and aged lubricants in SC, SF, SG, SJ and SL category, respectively. It was clearly shown that the trends of apparent activation energy increased from low to high conversion levels because long chain hydrocarbons remained in the base oil degraded at high activation energy [35]. Moreover, the average of the apparent activation energy of 5 categories in all fresh motor oils was higher than the aged lubricants. This showed that fresh lubricants are more stable than aged lubricants because chemical structures of base oils change from long chain hydrocarbons to aromatic compound during long exposure to high temperature for long period. Moreover, straight chains are substituted by aromatic rings and decrease the oxidative stability of lubricants [36-37].

Table 2. Activation energies determined of fresh and aged lubricants using Kissinger-Akahira-Sunose method in the API SC grade

| Conversion | Activation energy (kJ/mol) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | SC1 | | SC2 | | SC3 | | SC4 | | SC5 | |
| | fresh | aged | fresh | aged | fresh | aged | fresh | aged | fresh | aged |
| 0.1 | 91.98 | 90.43 | 78.81 | 74.87 | 89.79 | 80.39 | 86.12 | 83.84 | 77.67 | 75.04 |
| 0.2 | 92.04 | 88.94 | 78.77 | 76.62 | 99.40 | 89.61 | 98.77 | 87.04 | 87.97 | 84.56 |
| 0.3 | 93.57 | 90.99 | 80.95 | 79.26 | 105.91 | 98.35 | 100.05 | 95.92 | 95.81 | 88.84 |
| 0.4 | 92.48 | 89.08 | 83.12 | 82.61 | 104.56 | 96.63 | 99.58 | 97.13 | 98.20 | 92.56 |
| 0.5 | 98.85 | 95.07 | 85.58 | 84.08 | 106.85 | 99.40 | 105.66 | 102.79 | 102.38 | 99.34 |
| 0.6 | 97.28 | 96.23 | 88.49 | 87.36 | 115.48 | 107.92 | 106.22 | 104.76 | 104.05 | 98.83 |
| 0.7 | 100.57 | 99.77 | 91.02 | 88.64 | 113.49 | 105.34 | 107.58 | 106.73 | 107.69 | 103.28 |
| 0.8 | 103.21 | 102.94 | 94.46 | 91.04 | 116.18 | 109.10 | 112.96 | 110.62 | 112.95 | 107.06 |
| 0.9 | 107.99 | 106.79 | 98.65 | 96.13 | 119.19 | 113.43 | 114.62 | 113.12 | 118.99 | 114.41 |
| Mean | 97.55 | 95.58 | 86.65 | 84.51 | 107.87 | 100.02 | 103.51 | 100.22 | 100.63 | 95.99 |

Table 3. Activation energies determined of fresh and aged lubricants using Kissinger-Akahira-Sunose method in the API SF grade

| Conversion | Activation energy (kJ/mol) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | SF1 | | SF2 | | SF3 | | SF4 | | SF5 | |
| | fresh | aged | fresh | aged | fresh | aged | fresh | aged | fresh | aged |
| 0.1 | 84.59 | 79.61 | 75.38 | 72.27 | 85.35 | 78.04 | 82.22 | 74.52 | 85.08 | 78.40 |
| 0.2 | 96.90 | 92.50 | 83.62 | 79.99 | 93.71 | 86.64 | 89.01 | 87.94 | 94.39 | 86.97 |
| 0.3 | 97.03 | 95.48 | 87.35 | 84.48 | 97.91 | 90.75 | 91.33 | 86.02 | 99.89 | 91.85 |
| 0.4 | 100.60 | 97.90 | 90.18 | 87.41 | 106.98 | 94.99 | 93.42 | 89.02 | 103.17 | 95.88 |
| 0.5 | 104.80 | 101.20 | 93.08 | 90.38 | 105.17 | 98.69 | 96.48 | 91.29 | 106.74 | 98.51 |
| 0.6 | 107.80 | 103.70 | 96.20 | 92.34 | 109.12 | 101.32 | 100.95 | 93.77 | 110.14 | 103.26 |
| 0.7 | 110.80 | 106.80 | 98.65 | 95.14 | 112.72 | 109.67 | 101.56 | 97.09 | 115.71 | 107.84 |
| 0.8 | 115.40 | 110.10 | 100.92 | 98.84 | 116.67 | 108.43 | 104.76 | 99.73 | 122.91 | 120.76 |
| 0.9 | 118.20 | 114.90 | 104.57 | 102.33 | 121.33 | 113.14 | 108.37 | 103.04 | 137.86 | 134.84 |
| Mean | 104.01 | 100.24 | 92.22 | 89.24 | 105.44 | 97.96 | 96.46 | 91.38 | 108.43 | 102.03 |

Table 4. Activation energies determined of fresh and aged lubricants using Kissinger-Akahira-Sunose method in the API SG grade

| Con-version | Activation energy (kJ/mol) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | SG1 | | SG2 | | SG3 | | SG4 | |
| | fresh | aged | fresh | aged | fresh | aged | fresh | aged |
| 0.1 | 74.86 | 75.94 | 76.89 | 69.72 | 82.15 | 79.4 | 79.64 | 73.37 |
| 0.2 | 80.83 | 80.78 | 82.55 | 77.18 | 89.53 | 87.23 | 89.56 | 86.88 |
| 0.3 | 83.32 | 82.15 | 84.64 | 79.72 | 92.47 | 90.91 | 94.45 | 85.47 |
| 0.4 | 85.41 | 83.54 | 86.60 | 84.03 | 94.87 | 92.39 | 98.35 | 89.36 |
| 0.5 | 88.40 | 84.94 | 89.53 | 82.61 | 96.55 | 94.90 | 102.51 | 95.15 |
| 0.6 | 92.06 | 86.13 | 91.45 | 84.05 | 98.80 | 96.12 | 105.80 | 98.79 |
| 0.7 | 95.94 | 87.29 | 96.24 | 85.57 | 100.93 | 98.84 | 108.78 | 100.04 |
| 0.8 | 100.71 | 89.09 | 97.54 | 86.56 | 102.59 | 100.74 | 112.55 | 99.73 |
| 0.9 | 105.28 | 91.02 | 100.24 | 88.29 | 105.44 | 102.70 | 117.14 | 107.57 |
| Mean | 89.65 | 84.54 | 89.52 | 81.97 | 95.93 | 93.69 | 100.98 | 92.93 |

Table 2 showed activation energy results of SC group. SC3 and SC4 were the most stable oils in this group. At the initial condition, the average apparent activation energy of SC3 and SC4 were 107.87 and 103.51 kJmol$^{-1}$, respectively. After the degradation period, the average apparent activation energy of these 2 motor oils drops by approximately 8 and 3 kJmol$^{-1}$, respectively. SC1, SC2 had activation energy below 100 kJmol$^{-1}$ before the ageing period. After 8 weeks, activation energy decreased by approximately 2 kJmol$^{-1}$. SC5 decreased activation energy by approximately 5 kJmol$^{-1}$. After thermal degradation test, its activation energy was almost the same as that of the SC1.The apparent activation energy results indicate that a motor oil having higher activation energy is more stable than that with a lower average apparent activation energy [35]. Table 3 clearly indicated that SF5 was the most stable motor oil in SF group. The average apparent activation energy reached 108.43 kJmol$^{-1}$ at the fresh condition and dropped to 102.03 kJmol$^{-1}$ after 8 weeks of ageing test. SF1 and SF3 had quite a high activation energy at 104.01 and 105.44 kJmol$^{-1}$, respectively. However, the activation energy of SF2 and SF3 were not over 100 kJmol$^{-1}$. Especially, SF3 was the lowest stability in SF group. Table 4 showed the average apparent activation energy of SG grade. It indicted that after degradation test, SG3 and SG4 had the highest activation energy (93-94 kJmol$^{-1}$). However, when compared activation energy results at the fresh condition of 2 motors. SG4 had a significantly greater value than SG3 by approximately 5 kJmol$^{-1}$. This shows that SG3 was the most stable motor oil in SG group. The apparent activation energy of SJ and SL grades were listed in Table 5 and 6, respectively.

Table 5. Activation energies determined of fresh and aged lubricants using Kissinger-Akahira-Sunose method in the API SJ grad

| Con-version | Activation energy (kJ/mol) | | | | | |
|---|---|---|---|---|---|---|
| | SJ1 | | SJ2 | | SJ3 | |
| | fresh | aged | fresh | aged | fresh | aged |
| 0.1 | 84.02 | 79.82 | 81.66 | 75.73 | 82.37 | 78.31 |
| 0.2 | 89.83 | 83.87 | 89.03 | 83.06 | 88.67 | 82.98 |
| 0.3 | 95.93 | 88.74 | 94.51 | 88.55 | 91.66 | 84.05 |
| 0.4 | 102.23 | 92.38 | 100.39 | 91.94 | 94.18 | 85.91 |
| 0.5 | 108.28 | 97.92 | 104.69 | 99.32 | 95.90 | 87.63 |
| 0.6 | 113.86 | 103.62 | 109.19 | 103.16 | 98.28 | 89.94 |
| 0.7 | 120.25 | 107.42 | 117.58 | 108.41 | 100.25 | 91.98 |
| 0.8 | 128.72 | 112.92 | 117.58 | 114.87 | 104.38 | 95.19 |
| 0.9 | 136.93 | 121.98 | 122.41 | 121.18 | 110.86 | 101.22 |
| Mean | 108.89 | 98.74 | 104.12 | 98.47 | 96.28 | 88.58 |

SJ1 and SJ2 were more stable than SJ3 for fresh motor oil. After degradation, they had a similar average apparent activation energy of 98-99 kJmol$^{-1}$. However, at fresh condition SJ1 had higher average apparent activation energy than SJ2 by approximately 5 kJmol$^{-1}$. In SL group, ageing condition of SL3 exhibited the most stable lubricant in this group and showed the highest activation energy among 19 motor oils (average activation energy = 104.2 kJmol$^{-1}$). In fresh condition, the activation energy of SL3 was very high (108.92 kJmol$^{-1}$) while SL1 and SL2 were 103.72 and 106.08 kJmol$^{-1}$, respectively. After the degradation period, SL3 decreased its average activation energy only by 4 kJmol$^{-1}$ while SL1 and SL2 lost activation energy by approximately 8 and 21 kJmol$^{-1}$.

Table 6. Activation energies determined of fresh and aged lubricants using Kissinger-Akahira-Sunose method in the API SL grade

| Conversion | Activation energy (kJ/mol) | | | | | |
|---|---|---|---|---|---|---|
| | SL1 | | SL2 | | SL3 | |
| | fresh | aged | fresh | aged | fresh | aged |
| 0.1 | 79.68 | 72.92 | 82.25 | 66.78 | 95.18 | 90.26 |
| 0.2 | 84.06 | 80.09 | 92.46 | 75.38 | 98.88 | 95.01 |
| 0.3 | 95.57 | 86.78 | 97.75 | 78.98 | 100.56 | 97.23 |
| 0.4 | 99.92 | 91.45 | 102.22 | 83.07 | 103.88 | 99.97 |
| 0.5 | 104.69 | 97.21 | 107.29 | 85.61 | 107.05 | 105.56 |
| 0.6 | 108.12 | 98.61 | 112.29 | 89.09 | 112.31 | 109.25 |
| 0.7 | 113.83 | 103.18 | 116.79 | 92.68 | 118.31 | 114.59 |
| 0.8 | 119.56 | 111.77 | 120.52 | 95.70 | 120.79 | 116.51 |
| 0.9 | 128.09 | 118.18 | 123.12 | 98.41 | 123.33 | 119.39 |
| Mean | 103.72 | 95.58 | 106.08 | 85.08 | 108.92 | 105.31 |

The activation energy analysis of fresh and aged motor oils can be used to characterize the stability of lubricants. This study showed that there was no correlation between the activation energy and lubricant grades. The differences of the apparent activation energy depend on a formulation of base oils and additives present in motor oil. These variations can be attributed to the complex organic transformations occurring during degradation of the motor oil [35]. These components such as base oil, antioxidants, detergent, corrosion inhibitors, viscosity index improvers, anti-wear agents, and anti-foaming agents are important factors and impact to the changes in the apparent activation energy of motor oils. Determination of stability by using the apparent activation energy during thermal degradation process provide a better understanding in physiochemical properties of motor oils.

## 4. Conclusions

The results of these studies can be used to characterize the performance of motor oils. Good oxidative stability of lubricants had high OOT, OIT, and the activation energy while volatility loss was low. Using the common DSC to determine OIT and OOT were very useful for evaluation of the oxidative stability in lubricants. The TGA Noack test provided valuable information on volatilities of lubricant. It simulated real life conditions, which lubricant exposed to a high temperature and air. Volatility measured by Noack did not correlate well with the SAE viscosity and the API categories. Moreover, mass loss data of TGA can be used to calculate the apparent activation energy. This is an important tool for stability study.

These lubricant properties shown from this work are practical and powerful indicators for characterization performance of lubricant products in the market.

- Oxidative degradation was critical information to determine a performance of motor oils.
- The SAE viscosity and the API category were not good factors to determine the volatility of commercial motor oils.
- The latest API category (SL) were more stable than the previous categories (SC, SF, SG, and SJ).
- Lubricants with the same SAE viscosity and API category could show significant differences in their oxidative stability and volatility.
- Stability of lubricant can also be evaluated in term of the activation energy, and there is no correlation between the activation energy and API grades.

- The ageing test is important to physiochemical degradation study of motor oils. These thermal analysis applications such as OIT, OOT, volatility and the activation energy can be used for stability determination.

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### References

[1] Ng W, Law H. The New Lubricant Trade in ASEAN. Ipsos Business Consulting. 2015; 1-9.
[2] Madanhire I, Mbohwa C. Mitigating Environmental Impact of Petroleum Lubricants, Springer; 2016; Chapter 2; 17-34.
[3] Stepina V, Vesely V. Lubricants and special Fluids, 1st ed.; Elsevier; 1992; Chapter 2; 63-68.
[4] Ebert LB. Chemistry of Engine Combustion Deposits, L.B. Ebert., Ed.; Springer: Boston, 1985; Chapter 17; 289-302.
[5] Kök MV, Sztatisz J, Pokol G. High-Pressure DSC Applications on Crude Oil Combustion. Energy & Fuels 1997; 11(6): 1137-1142.
[6] Perez JM. Oxidative properties of lubricants using thermal analysis. Thermochimica Acta 2000; 357–358: 47–56.
[7] Gamlin CD, Dutta NK, Choudhury NR, Kehoe D, Matisons J. Evaluation of kinetic parameters of thermal and oxidative decomposition of base oils by conventional, isothermal and modulated TGA and pressure DSC. Thermochimica. Acta 2002; 392–393: 357–369.
[8] Crnkovic PM, Leiva CRM, dos Santos AM, Milioli FE. Kinetic study of the oxidative degradation of Brazilian fuel oils. Energy Fuels 2007; 21(6): 3415–3419.
[9] Blaine LR. Thermal analytical characterization of oils and lubricants. American Laboratory 1994; 18(1): 18–20.
[10] Peltzer M, Jiménez A. Determination of oxidation parameters by DSC for polypropylene stabilized with hydroxytyrosol (3,4-dihydroxy-phenylethanol). Journal of Thermal Analysis and Calorimetry 2009; 96(1): 243–248.
[11] Volponi, JE, Mei LHI, Rosa DS. Use of oxidation onset temperature measurements for evaluating the oxidative degradation of isotatic polypropylene. Journal of Polymers and the Environment 2004; 12(1): 11–16.
[12] Tarrío-Saavedra J, Naya S, López-Beceiro J, Gracia-Fernández C, Artiaga R. Thermooxidative properties of biodiesels and other biological fuels. Biodiesel- Quality, Emissions and By-Products, 1st ed.; InTech, 2011; Chapter 3; 55-59.
[13] Pirjola L, Karjalainen P, Heikkilä J, Saari S, Tzamkiozis T, Ntziachristos L, Kulmala,K, Keskinen J, and Rönkkö T. Effects of Fresh Lubricant Oils on Particle Emissions Emitted by a Modern Gasoline Direct Injection Passenger Car. Environmental Science & Technology 2015; 49(6): 3644-3652.
[14] Zinbo M, Skewes LM. Determination of engine oil volatility by thermogravimetry. Thermochimica Acta 1989; 154(2): 367-376.
[15] Standard Test Method for Evaporation Loss of Lubricating Oils by Thermogravimetric Analyzer (TGA) Noack Method. ASTM D6375-09
[16] Focke WW, Westhuizen IVD, Grobler ABL, Nshoane K.T, Reddy J.K, Luyt A.S. The effect of synthetic antioxidants on the oxidative stability of biodiesel. Fuel 2012; 94: 227-233.
[17] Standard Test Methods for Determining Oxidation Induction Time of Hydrocarbons by Differential Scanning Calorimetry. ASTM E1858-00
[18] Standard Test Methods for Oxidation Onset Temperature of Hydrocarbons by Differential Scanning Calorimetry. ASTM E2009-08
[19] Kök MV, Pamir MR. Non-Isothermal Pyrolysis and Kinetics of Oil Shales. Journal of Thermal Analysis and Calorimetry 1999; 56(2): 953-958.
[20] Crnkovic PM, Leiva CRM, dos Santos AM, Milioli FE. Kinetic study of the oxidative degradation of Brazilian fuel oils. Energy & Fuels 2007; 21(6): 3415-3419.
[21] Ichiro M. Molecular Science of Lubricant Additives. Applied Sciences 2017; 7(5): 445.
[22] Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda L.A, Popescu C, Sbirrazzuoli, N. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. Thermochim. Acta 2011; 520(1-2): 1–19.

[23] Santos JCO, dos Santos IMG, Souza AG, Sobrinho EV, Fernandes VJ, Silva AJN. Thermoanalytical and rheological characterization of automotive mineral lubricants after thermal degradation, Fuel 2004; 83(17–18): 2393-2399.

[24] Lim ACR, Chin BLF, Jawad ZA, Hii KL. Kinetic Analysis of Rice Husk Pyrolysis Using Kissinger-Akahira-Sunose (KAS) Method. Procedia Engineering 2016; 148: 1247-1251.

[25] Vyazovkin S, Burnham A.K, Criado J.M, Pérez-Maqueda LA, Popescu C, Sbirrazzuoli N. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. Thermochim. Acta 2011; 520: 1–19.

[26] Mayo FR. Free radical autoxidations of hydrocarbons. Accounts of Chemical Research 1968; 1(7): 193-201.

[27] Černý J, Zelinka M. Oxidative stability of Lubricants Measured by a PDSC Technique. Pet Coal 2004; 46: 56-62.

[28] Fox MF. Chemistry and Technology of Lubricants, Mortier R, Fox M, Orszulik S.; Ed., Springer, 2010; Chapter 17; 512-527.

[29] Aguilar G, Mazzamaro G, Rasberger M. Chemistry and Technology of Lubricants, Mortier R, Fox M, Orszulik S.; Ed., Springer, 2010; Chapter 4; 140-146.

[30] Adamczewska J, Love C. Oxidative stability of lubricants measured by PDSC CEC L-85-T-99 test procedure. Journal of Thermal Analysis and Calorimetry 2005; 80(3): 753–759.

[31] Wu Y, Weimin L, Zhanga M, Wang X. Improvement of oxidative stability of trimethylolpropane trioleate lubricant. Thermochimica Acta 2013; 569: 112-118.

[32] Salih N, Salimon J, Yousif E, Abdullah BM. Biolubricant basestocks from chemically modified plant oils: ricinoleic acid based-tetraesters. Chemistry Central Journal 2013; **7**: 128-141.

[33] Rudnick LR. Additives for industrial lubricant applications, 2nd ed,; CRC Press, 2009; Chapter 26; 493-506.

[31] Rudnick LR, Buchanan RP, Medina F. Evaluation of oxidation-mediated volatility of hydrocarbon lubricant base fluids, Synthetic Lubrication 2006; 23(1): 11–26.

[35] Tripathi AK, Vinu R. Characterization of thermal stability of synthetic and semi-synthetic engine oils. Lubricants 2015; 3(1): 54-79.

[36] Adhvaryu A, Perez JM, Singh ID. Application of quantitative NMR spectroscopy to oxidation kinetics of base oils using a pressurized differential scanning calorimetry technique. Energy Fuels 1999; 13(2): 493–498.

[37] Vinu R, Broadbelt LJ. Unraveling reaction pathways and specifying reaction kinetics for complex systems. Annual review of chemical and biomolecular engineering. 2012; 3: 29–54.

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