Thermal stability evaluation of palm oil as energy transport media

W.B. Wan Nik [a,*], F.N. Ani [b], H.H. Masjuki [c]

[a] *Faculty of Science and Technology, Kolej Universiti Sains dan Teknologi Malaysia, Mengabang Telipot, 21030 Kuala Terengganu, Malaysia*
[b] *Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia*
[c] *Department of Mechanical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia*

Abstract

The thermal stability of palm oil as energy transport media in a hydraulic system was studied. The oils were aged by circulating the oil in an open loop hydraulic system at an isothermal condition of 55 °C for 600 h. The thermal behavior and kinetic parameters of fresh and degraded palm oil, with and without oxidation inhibitor, were studied using the dynamic heating rate mode of a thermogravimetric analyser (TGA). Viscometric properties, total acid number and iodine value analyses were used to complement the TGA data. The thermodynamic parameter of activation energy of the samples was determined by direct Arrhenius plot and integral methods. The results may have important applications in the development of palm oil based hydraulic fluid. The results were compared with commercial vegetable based hydraulic fluid. The use of F10 and L135 additives was found to suppress significantly the increase of acid level and viscosity of the fluid.
© 2004 Elsevier Ltd. All rights reserved.

Keywords: Thermal analysis; Hydraulic fluid; Kinetics; Palm oil

---

* Corresponding author. Tel.: +60 966 833 42; fax: +60 966 946 60.
E-mail address: niksani@kustem.edu.my (W.B. Wan Nik).

1. Introduction

The usage of environmentally benign products as lubricants has many advantages. Some of the positive points are high biodegradability, no toxicity to living organisms and no pollution to water, soil and air. A good choice for benign raw material is vegetable based oil. This base material is derived from a renewable resource. Vegetable oils have already been considered as potential industrial fluids as early as the 1900s. The early use of vegetable oils as an industrial component includes use as a coolant in power capacitors and electrical transformers in the 1990s. However, the use was merely experimental rather than commercial [1]. The interest in using this type of oil decreased due to its several disadvantages in industrial applications such as oxidation and thermal stability. Furthermore, these oils have less economic advantages since the price is at least twice as much as petroleum based oil. Thus, later, these oils were used mainly as foodstuff.

However, due to the increase in environmental awareness lately, research in converting vegetable based oil into non-food applications has revived. The research includes the potential use of this base oil as hydraulic fluids, surfactants, solvents, drilling fluid, transmission fluid and lubricants. The base oil can also be converted to an oleochemical product before being tested in an engine or industrial machines [2–6]. Vegetable or plant oil was considered the most likely candidate for a fully biodegradable hydraulic fluid. Plant oil is a natural resource available in abundance. It is a good power transmission medium, lubricating agent and corrosion protection agent.

1.1. Hydraulic fluid

A hydraulic fluid must perform several functions. The prime functions are energy transmission and lubrication. During energy conversion, the electrical energy is converted to mechanical power at the motor-pump shaft. In a positive displacement pump, the mechanical energy is then converted to fluid energy. At an actuator, the fluid energy is finally converted back to mechanical energy to perform designated mechanical tasks. In performing its duty, the fluid must be thermally stable and be able to protect hydraulic components from corrosion. Commercial hydraulic fluid is already fortified with additive packages to increase the fluid's useful lifetime and to meet increasingly demanding industrial requirements. The base oil is blended with commercial additives from 0.1% to as high as 10%.

Some hydraulic systems use hundreds of liters, while some others use only several litres of hydraulic fluid. The hydraulic reservoir comes in different sizes: large, medium and small tanks with vent or sealed types. The smaller reservoirs are more widely available than the larger units because many hydraulic systems are used for mobile applications. Compact and small reservoirs are preferred to reduce the weight of the vehicle. When used on a vehicle, a fire resistance fluid is preferred. The fluid should have high viscosity index, flash and fire points. This is some of the reasons why vegetable based oil should be used as hydraulic fluid for several applications. Furthermore, in recent years, environmental concerns have been raised by consumers and producers so as not to contaminate the surroundings. Contamination of the planting soil is as serious as contamination of the water supply.

1.2. Palm oil and palm based hydraulic fluid project

Malaysia is not only the largest producer but also the largest exporter of palm oil in the world. It is the main income for Malaysia. For example, the Malaysian export of palm oil products increased from US $6.5 billion in 2000 to nearly US $7.5 billion in 2001 [7]. Palm oil consists of mainly glycerol ester and fatty acids. Currently, it is used mostly for edible purposes such as cooking oil. The remainder is used for production of oleochemical, margerine, soap and animal feed raw material.

Since there is abundant palm oil to be processed, a lot of palm oil refineries and oleochemical companies are in operation in Malaysia. In order to extract the oil from the mesocarp, shell and kernel, several types of hydraulic systems are used to press the oil out. Some operators use commercial hydraulic oil, while some others use palm oil in their hydraulic system. Different operators use different grades of palm oil available in their processing plants. To ensure the oil will not harm the hydraulic components, especially the seals and hoses, they regularly change the oil.

Because of the above reasons, the palm based hydraulic fluid project was initiated a few years ago in Kolej Universiti Sains dan Teknologi Malaysia (KUSTEM). Technical support was obtained from the Universiti Teknologi Malaysia (UTM), Universiti Malaya (UM) and Malaysian Palm Oil Board. It was decided to use palm oil in the study, since it is widely planted in Malaysia. Diversification of palm oil use is crucial in order to maintain and secure the palm oil price. However, the researchers at KUSTEM, UTM and UM agree that the oil needed further improvement before it is used as a hydraulic fluid.

The purpose of this paper is to present the kinetic evaluation results of palm oil when it was heated and sheared in a hydraulic system. The effect of anti-oxidants on the oil stability was investigated. The results were compared with those of commercial, vegetable based hydraulic fluid. The rate of oil decomposition and degradation depends not only on the type of anti-oxidant but also on the anti-oxidant amount.

2. Materials and methods

2.1. Oil sample and additives

The palm oil was obtained from a refinery in the state of Johor. The oil is refined, bleached and deodorized palm oil. It is processed for cooking oil and constituents for margarine and shortening. The fatty acid composition for the palm oil used, as measured by gas chromatography, is shown in Table 1.

Commercial vegetable based hydraulic fluid was imported from overseas about one year ago in 18l containers. Before use, it was stored in a dark cabinet at room temperature. The properties of the hydraulic fluid are given in Table 2.

The Irgalube F10 and Irganox L135 additives were supplied by Ciba Specialty Chemicals, Inc. Irgalube F10 is normally used as a friction modifier and anti-oxidant for engine oil, while Irganox L135 is a high molecular weight phenolic anti-oxidant normally used for lubricating oils. The chemical structures of the additives used are shown in Fig. 1. These additives were selected based on their good performance in our previous oven tests.

Table 1
Fatty acid components of palm oil used

Common name	Systematic name	Symbol	Percentage of total weight
Saturated acids			
Lauric	*n*-Dodecanoic	C12:0	0.4
Myristic	*n*-Tetradecanoic	C14:0	1.0
Palmitic	*n*-Hexadecanoic	C16:0	38.3
Stearic	*n*-Octadecanoic	C18:0	4.0
Arachidic	*n*-Eicosanoic	C20:0	0.7
Mono-unsaturated acids			
Palmitoleic	*n*-Hexadec-9-enoic	C16:1	0.4
Oleic	*n*-Octadec-9-enoic	C18:1	43.1
Gadoleic	*n*-Eicos-9-enoic	C20:1	0.1
Poly-unsaturated acids			
Linoleic	*n*-Octadec-9, 12-dienoic	C18:2	11.6
Linolenic	*n*-Octadec-9, 12, 15-trienoic	C18:3	0.2

Table 2
The properties of the hydraulic fluid

Property	Testing method	Unit	
Physical property			
Density	ASTM D-1298-85	kg/m^3	920
Pour point	ASTM D-97-93	°C	−34
Flash point	ASTM D-92-90	°C	294
Energy content	ASTM D-240-92	kJ/kg	39,490
Chemistry property			
Total acid number	ASTM D-664-89	mg KOH/g	0.62
Iodine value	AOCS Cd 1b-87	cg I$_2$/g	87.66
Saturated acids	AOCS CE2-66	%	7.8
Mono-unsaturated acids	AOCS CE2-66	%	63.0
Poly-unsaturated acids	AOCS CE2-66	%	28.4

The samples used were palm oil blended with the different types and percentages of additives. Eighteen litres of palm oil blended with the additives were contained in a cylindrical reservoir. Thermal degradation of the oil samples was examined by circulating the oil in a 4 m length of pipe by means of a Yuken positive displacement pump. The oil temperature in the hydraulic system was maintained at 55 °C by a cooling system. The total investigation period was 600 h. After each oil type was tested, the system was flushed thoroughly using the next oil sample until no trace of the previous oil was noticed. The new fresh oil sample was then poured into the reservoir.

The acid value and viscosity of the oil were monitored regularly. Twenty millilitre samples were drawn at 0, 100, 200, 300, 400, 500 and 600 h intervals. The iodine value was determined, and TGA tests were performed before and after the end of the heating exposure period.
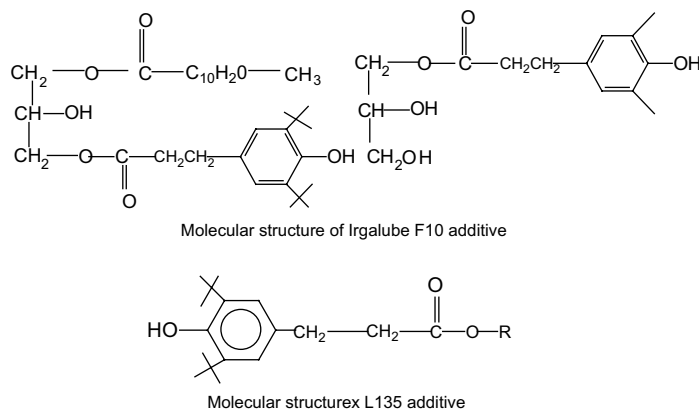
Fig. 1. Molecular structure of additives used. (a) Molecular structure of Irgalube F10 additive and (b) molecular structure of Irganox L135 additive.

2.2. Thermal analysis

The thermogravimetric (TG) thermogram was recorded on the thermogravimetric analyser Perkin Elmer Pyris 6. The thermal analysis was conducted with a heating rate of $5\,°C/min$ from $50\,°C$ to $500\,°C$ in a nitrogen flow of $20\,ml/min$. A sample size of about $15\,mg$ was used. The temperature and weight scales were calibrated using indium over a specific range of heating rates with a calibration parameter over its respective Curie point.

2.3. Viscosity, total acid number and iodine value

The viscosity of the oil was measured using a Brookfield Viscometer (Brookfield Laboratories USA, model DV-I+) with spindle number 18. Thermosel was used so that the oil viscosity at different temperatures can be measured. Up to 10 different speeds were used for each temperature. The measurement was performed in triplicate.

The total acid value (TAN) was determined by potentiometric titration according to the ASTM method D664–89 using a Methrohm titrator, while the iodine value (IV) was determined as per AOCS method Cd 1b–87.

3. Theoretical background

3.1. Thermal analysis

The thermal stability of the oil can be one of the important properties in the use of hydraulic oil, especially for high temperature application such as a fire resistant fluid. There are several methods available to evaluate the thermal stability of oils. Thermal analytical methods include a group of techniques in which the thermal behavior or properties of a material are measured as a function of temperature. This technique of analysis is the preferred and accepted method

since it provides fast assessment and only a small amount of sample is required. Thermal analysis is very useful in both quantitative and qualitative analyses. Oil samples can be identified, quantified and characterized during the oil thermal investigation. The thermal tests involve weight and enthalpy change as the sample is heated.

Initially, TGA has been used extensively in polymer chemistry for measurement of polymer degradation [8–10]. The apparatus continuously monitors the changes of sample weight while the sample is being heated in an isothermal or dynamic condition.

3.2. Non-isothermal analysis

Thermogravimetric data was used in characterizing the materials as well as in investigating the thermodynamics and kinetics of the reactions and transitions that result from the application of the oil samples. Currently, several methods are available in the literature that can be used to calculate the kinetic parameters. The kinetic analysis used for the thermal conversion of the oil is similar to that reported by Torrene and Galan [11] and Jaber and Probert [12].

The rate of conversion, dx/dt, for the oil conversion is expressed by

$$\frac{dx}{dt} = kf(x) = k(1-x)^n \tag{1}$$

where n is the order of reaction, k is the reaction rate constant and x is the extent of conversion or fractional weight loss, given by

$$x = \frac{w_o - w_t}{w_o - w_\infty}$$

where w_o, w_t and w_∞ are the original, current and final weights, respectively.

Based on the TGA thermogram, it was found that the reaction can be estimated as first oder, thus $n = 1$ and Eq. (1) becomes

$$\frac{dx}{dt} = k(1-x).$$

For the non-isothermal case, the above equation can be further modified to

$$\frac{dx}{dT} \cdot \frac{dT}{dt} = k(1-x) \tag{2}$$

where $\frac{dT}{dt}$ is the heating rate B.

According to the Arrhenius relationship, the reaction rate constant k in Eq. (2) can be expressed as

$$k = A \exp(-E_a/RT). \tag{3}$$

Substituting Eq. (3) into Eq. (2) yields

$$\frac{dx}{dt} = \frac{A}{B} \exp\left(\frac{-E_a}{RT}\right)(1-x). \tag{4}$$

In this study, two models were used to evaluate the kinetic parameters of the oil samples. For the direct Arrhenius plot method for the non-isothermal kinetic parameters with constant heating rate ($B = dT/dt$), Eq. (4) was rearranged to

$$\ln\left[\frac{1}{(1-x)}\frac{dx}{dt}\right] = \ln\frac{A}{B} - \frac{E_a}{RT}. \tag{5}$$

The plot $\ln[\frac{1}{(1-x)}\frac{dx}{dt}]$ versus $1/T$ should give a straight line with slope $-E_a/R$, from which the activation energy, E_a, can be calculated.

The integration method determines the overall reaction from the conversion versus temperature curves. Rearranging, integrating and using a natural logarithm, Eq. (4) yields

$$\ln(-\ln(1-x)) = \ln\left[\frac{ART^2}{BE_a}\left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT}. \tag{6}$$

The plot $\ln[-\ln(1-x)]$ versus $1/T$ should give a straight line with slope $-E_a/R$, from which the activation energy E_a, can be calculated.

4. Results and discussion

Oil circulated in the simple piping system was heated due to friction at the pump, loading valve and 400 cm of pipings. The friction gave rise to a temperature of 55 °C or more. The excess heat was taken away by the cooling system, so as to keep the oil in the hydraulic reservoir at 55 °C at all times. The following section discusses the TGA and conventional methods in evaluating the oil properties drawn from the reservoir.

4.1. Thermal analysis

Thermogravimetric analysis has been widely used to evaluate the thermal stability of many types of materials such as polymers and oils. The thermal properties or behavior of oil samples are measured as a function of various reaction parameters such as temperature, time and heating rates. This type of technique is a very popular approach in the chemical engineering field as a tool of thermal analysis.

Before introduction into the hydraulic system, the oil samples were charaterized and quantified using this TGA method. Kinetics of the palm oil samples were studied non-isothermally under conditions of sample temperature increasing at the rate of 5 °C/min. This TGA test involves a weight change as the oil was heated. The weight loss data of the sample was logged using the in situ computer. Fig. 2 shows the temperature scan of a typical pure palm oil sample in nitrogen atmospheric heating. It shows the decomposition and weight loss of the oil samples and derivative weight loss (DTG) with the corresponding temperature. The changes in weight occurred from the forming and breaking of the physical and chemical bonds at elevated temperatures. The figure reveals that the thermal degradation of the oil occurred in a single step reaction. Other samples gave similar TG–DTG curves.
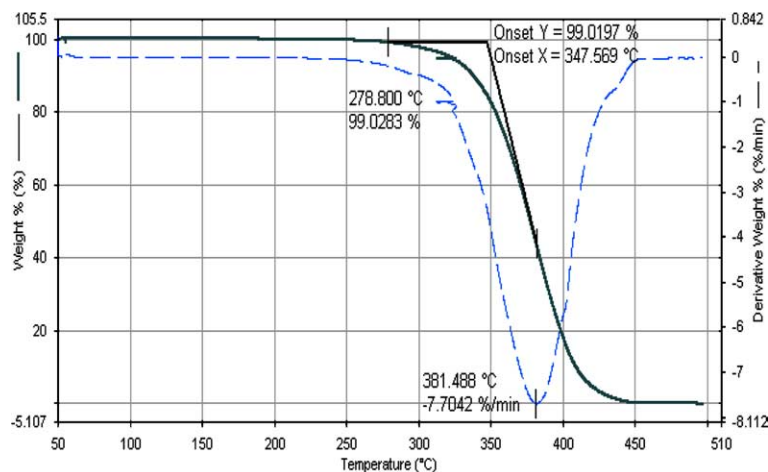
Fig. 2. Typical TGA thermogram for palm oil.

The oil thermogram shown in Fig. 2 consists of three phases. During the first phase, only a minimal weight change was observed during this induction period. The thermogram shows that the 1% weight loss of the pure palm oil sample in the inert atmosphere occurs around 279 °C. Forty-six minutes elapsed before it changed to the second phase. A rapid weight change was observed during the second phase. The maximum degradation rate occurred at a temperature of about 381 °C where the rate of weight decrease increased to the maximum up to this point. Slower weight decreases were observed at higher temperatures. The curve flattering at 466 °C shows that no further conversion was occurring.

The DTG curve shows clear evidence for the three degradation steps. The TG curves and the negative first derivative of the oil decomposition (Fig. 2) suggests that the overall process occurred in first order kinetics.

Onset temperatures (T_{on}) can be used to indicate the resistance of the oil to thermal degradation. This was determined by extrapolating the horizontal baseline at 1% degradation. The intercept of this line with the tangent to the downward portion of the weight curve was defined as the onset temperature.

Table 3 shows the details for the point of 1% weight loss temperature, onset temperature, offset temperature and final temperature. The onset temperature for the fresh oil A (no additive) is significantly lower than that of the oils with additive (B, C, D). This shows that the additives used in this study managed to protect the oil from oxidation. Hindered phenol is among the earliest oxidation inhibitor packages suggested. In our case, we use L135, a phenolic anti-oxidant. It works as a free radical scavenger. However, the onset temperature of oil with L135 additive is lower than that of the oil with F10 additive of the same percentage. The onset temperatures for A and E of the aged cases are very similar while those for the samples with additive are slighly higher.

Surprisingly, the T_1 for the E samples, both fresh and aged, were significantly low, aged being lowest. This indicates the presence of small amounts of volatile components in the oil. After being aged in the hydraulic system, the T_1 of the aged A sample was greatly reduced, similar to the observation for sample E. This could be attributed to decomposition of volatile components that were produced during the heating process.

Table 3
The effect of anti-oxidant on degradation temperatures of palm and hydraulic oils for 0 and 600h samples

Sample id.	Additive and amount	Temperature at 1% weight loss T_1 (°C)	Onset temperature T_{on} (°C)	Offset temperature T_{off} (°C)	Final temperature T_f (°C)
A_0	PO, no additive	278.80	347.57	426.55	465.92
B_0	PO + 1.5% F10	215.09	384.48	435.84	469.85
C_0	PO + 2% F10	266.56	384.64	430.98	464.78
D_0	PO + 1.5% L135	244.505	375.99	433.00	466.50
E_0	HO	176.22	376.47	436.28	473.29
A_{600}	PO, no additive	134.23	331.94	434.02	465.04
B_{600}	PO + 1.5% F10	224.87	377.78	433.77	460.59
C_{600}	PO + 2% F10	242.81	375.84	435.90	462.56
D_{600}	PO + 1.5% L135	258.46	373.51	436.35	466.54
E_{600}	HO	49.575	363.03	443.12	478.22

Comparing the 0 and 600h values, it can be seen that the T_{on} values for all the fresh samples were 2–16 °C higher than those of the aged oil. This is as expected. The degraded oil may have amounts of higher volatility components that lead to earlier decomposition. Naturally, the more the volatile degradation product, the lower the onset temperature. Similar results occurred for polyfilms that were degraded for several weeks [13].

Fig. 3 shows the extent of conversion of the fresh and aged oils at corresponding temperatures. Significant differences of the conversion curve exist for the fresh and aged palm oils without additive. The aged oil starts to pyrolyse at a lower temperature than the fresh oil. Besides decomposition of the degraded volatile product, this also might be due to vaporization of the water content. The aged oil had 1758 ppm water content when measured according to ASTM D4377. The fresh oil had only 994 ppm of water. At elevated temperatures, the aged oil also has a higher fractional weight loss. This is due to pyrolysis of the volatile secondary product that was produced during the 600h heating period.
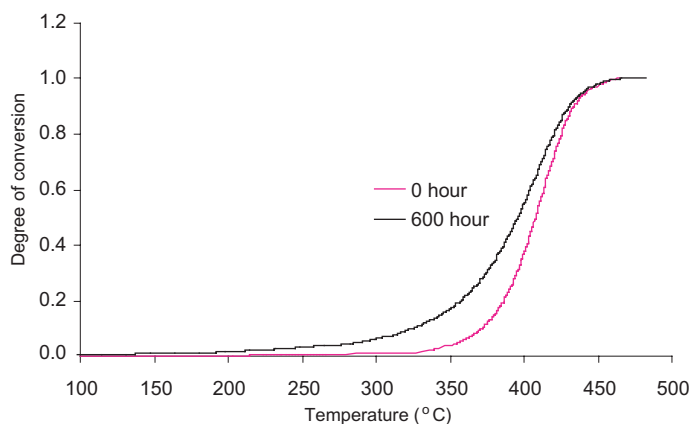

Fig. 3. Conversion versus temperature of palm oil without additive.

A similar pyrolysis pattern was observed using the E oil. This shows that this oil degraded to a similar degree as oil A. Other complementary tests (will be discussed later) show that the A and E oils had been badly degraded, while the introduction of the additive has greatly improved the degradation rate. The conversion pattern of C oil is shown in Fig. 4. The fractional weight loss of the aged oil closely tracks that of the fresh oil. The conversion patterns of the B and D oils are similar to those with C. The similar tracks for the B, C and D oils show that the oils were not much degraded compared to oil A or E. The results obtained for the stable (B, C, D) and unstable (A, E) oils indicate that the fractional weight loss vs reaction temperatures for new and used oil can be used to indicate the oil degradation condition.

Thermogravimetric analysis using the direct Arrhenius plot method has been used by numerous researchers. Eq. 5 was used to determine the activation energy of the oil samples by the direct Arrhenius plot method. The values of x and dx/dT were calculated using an Excel spreadsheet. The plot was made of $\ln[1/(1-x).\frac{dx}{dt}]$ versus $1/T$ for the oil decomposition. Fig. 5 presents the Arrhenius plot of the oil samples that was used to calculate the kinetic parameters such as activation energy and frequency factor. The figure shows a linear relationship of $\ln[\frac{1}{(1-x)}\frac{dx}{dt}]$ versus $1/T$ for all samples. This linear relationship again indicates that the oil conversion reaction can be treated as a first order reaction. Thus, the kinetic parameter constants at increasing temperature can be determined from the graph slope with high accuracy.

The calculated best fitting straight line in Fig. 5 describes the oil decomposition. With the linear regression of the abscissa and ordinate parameters, the slopes and intercepts of the lines in the figure indicate the values of the activation energy E_a and frequency factor A, respectively. For this sample, the energy of activation and the frequency factor were computed to be 181 kJ/mol and $5.48E \times 10^{12}$ min^{-1}, respectively.

Table 4a and b compare the activation energy and frequency factors for all the fresh and aged palm oil samples, respectively. The apparent activation energy of palm oil without additive was about 181 kJ/mol, while the activation energy for the blended samples was increased by 23–34 kJ/mol. Based on the activation energy of fresh oil, the F10 additive is better than L135. The onset temperature discussed earlier shows a similar pattern. The influence of the same amount
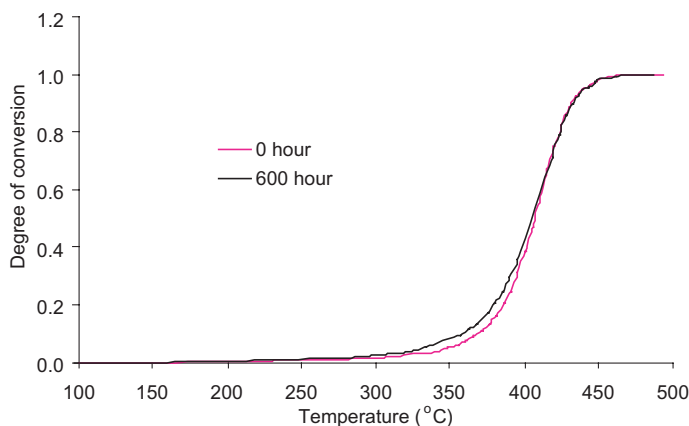

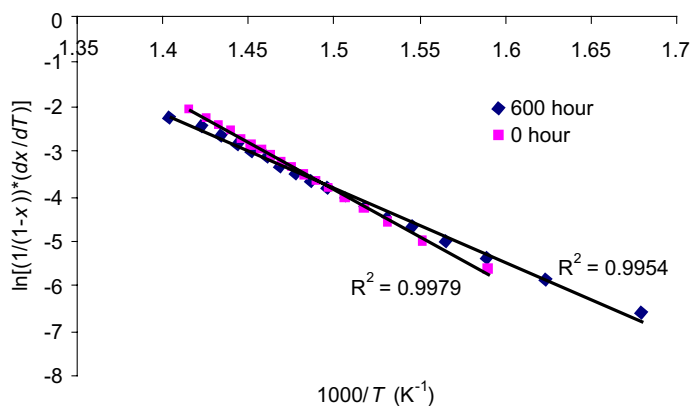Fig. 4. Conversion versus temperature of palm oil with additive.

Fig. 5. Arrhenius plot for fresh and aged palm oil.

Table 4
Panel A: Kinetic parameter for palm oil with and without additive 0 h. Panel B: Kinetic parameter for palm oil with and without additive 600 h

Sample id.	Sample size (mg)	Activation energy, E_a (kJ/mol)	Frequency factor, A (min^{-1})
Panel A			
A	14.880	180.56	5.48×10^{12}
B	15.539	207.77	1.39×10^{15}
C	14.733	214.07	4.55×10^{15}
D	14.903	203.47	6.85×10^{14}
Panel B			
A	14.609	138.57	7.80×10^{9}
B	14.675	195.94	1.90×10^{14}
C	15.947	192.32	9.46×10^{13}
D	15.793	188.14	4.61×10^{13}

of F10 and L135 additives increases the activation energy by 27 and 23 kJ/mol, respectively. Increasing the F10 additive amount from 1.5% to 2% increases the activation energy from 207.77 to 214.07 kJ/mol. The activation energy for both the palm oils and commercial oil were reduced after being heated and sheared in the hydraulic system.

The frequency factor has similar behavior to that of the activation energy. The frequency factor for *A* is the smallest for both the 0 and 600 h cases, while *C* has the highest frequency factor for the 0 h case and the second highest for the 600 h case. This shows that the additive amount has some effect on the frequency factor. Increasing the additive amount from 1.5% to 2% increases the frequency factor to 4.55×10^{15} from 1.39×10^{15} min^{-1}. The table also shows that all the aged samples experienced decreases in frequency factor compared to those of the fresh samples. Similar resuts were observed for commercial oil *E* (Table 5).

In order to ensure sample temperature uniformity, approximately the same (15 mg) sample size was used in the experiments. This was to reduce the resulting error. It is expected that the onset, 1% weight loss and final temperatures would decrease or increase if smaller or larger sample sizes

Table 5
Kinetic parameter for commercial oil at 0 hour and 600 hour

Sample no.	Sample size (mg)	Activation energy, E_a (kJ/mol)	Frequency factor, A (min^{-1})
E_0	14.581	154.22	8.96×10^{12}
E_{600}	14.338	132.39	1.93×10^9

were used, respectively. Larger sample size means smaller surface exposure per sample volume. This would make the decomposition process slower.

The oil thermal stability could be defined as the resistance to thermal degradation. Thus, the thermal stability of the oils can be used as an indicator of their durability when used as an industrial hydraulic fluid. Actually, the operating temperature of a good hydraulic system is only between 35 and 55 °C. A 10 °C increase in temperature will shorten the oil life time to half. In order to accelerate the aging process, the 55 °C test temperature was chosen. In general, the life time of the oil deteriorates according to the extent of ageing. The higher the temperature, the faster is the oxidation process, i.e. degrading the oil. In this real hydraulic system test, the oil was not only exposed to heat but also to mechanical stress in the mechanical components and pipings and chemical interaction with degraded materials (broken oil seal etc.).

Fig. 6 shows the integral plot for fresh and aged palm oil without additive. As in Fig. 5, the 0 h case yields a higher slope compared to the 600 h case. Since the activation energy was calculated from the slope of the plot, this explains why fresh oils have higher activation energy compared to aged oils.

Table 6 compares the activation energy calculated using the direct Arrhenius method and the integral method. Except for the A 0 h and E 0 h, the activation energies for all the samples calculated using the direct Arrhenius method are larger than those obtained by the integral method. The activation energy values for the aged samples are always smaller those of the fresh samples. This is also true for the integral method. As can be seen from the table, almost all correlation
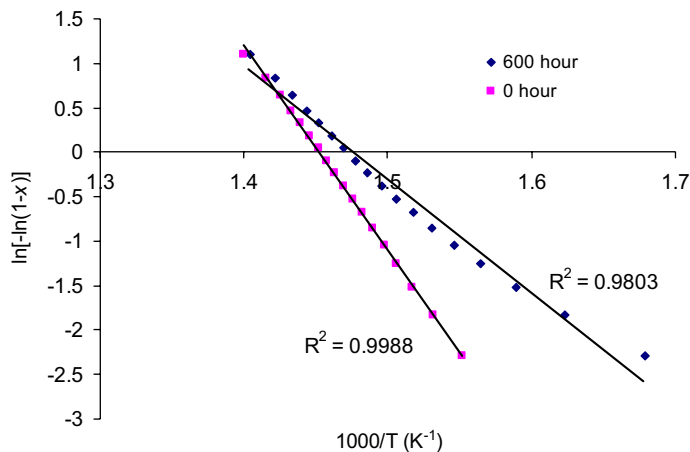

Fig. 6. Integral plot for fresh and aged palm oil.

Table 6
Activation energy calculated by integral and direct Arhenius methods

Sample id.	Integral	Correlation coefficient	Direct Arhenius	Correlation coefficient
A_0	188.85	0.9988	180.56	0.9979
A_{600}	106.19	0.9803	138.57	0.9954
B_0	188.85	0.9980	207.77	0.9849
B_{600}	158.74	0.9910	195.94	0.9973
C_0	191.83	0.9971	214.07	0.9822
C_{600}	173.09	0.9960	192.32	0.9954
D_0	203.47	0.9783	203.47	0.9783
D_{600}	154.52	0.9907	188.14	0.9940
E_0	161.65	0.9908	154.22	0.9205
E_{600}	108.20	0.9934	132.39	0.9264

coefficients by the direct Arrhenius and integral methods were close to unity, and in many cases, a higher correlation coefficient was obtained for the integral method.

The order of this reaction for the oil sample was calculated as $n = (y - B - Cx)/z$ [14], where

$$y = \ln\left\{\left(-\frac{1}{w_0 - w_\infty}\right)\left(\frac{dw}{dt}\right)\right\}$$

$$x = \frac{1}{RT}$$

$$z = \ln\left(\frac{w - w_\infty}{w_0 - w_\infty}\right)$$

$$B = \ln A$$

$$C = -E_a.$$

The multiple regression analysis was done using common statistical software. The input values were x, y and z and were calculated using Microsoft Excel. The result is shown in Fig. 7. It was found that for the palm oil samples, with or without additives, whether fresh or aged samples, the apparent order of the reactions n were in the range of 0.852–1.46. However, for the commercial hydraulic oil, the orders for the fresh and aged samples were 1.92 and 1.72, respectively. The high order number for E may be due to the complex formulation of the oil. A high coefficient of correlation ($r^2 > 0.99$) was obtained for each oil sample in this study.

The bar chart shows the values of order for all samples. It was found that the order decreased with heating time for all samples. Also we noticed that the order increases slightly with the addition of an additive, the more the additive, the higher was the order. Interestingly, the order reduction for A (palm oil without additive) is almost double that of the sample with additive. Not only the additive type but also the additive amount affects the order reduction. A higher amount of additive (oil C compared to oil B) reduces the order reduction.
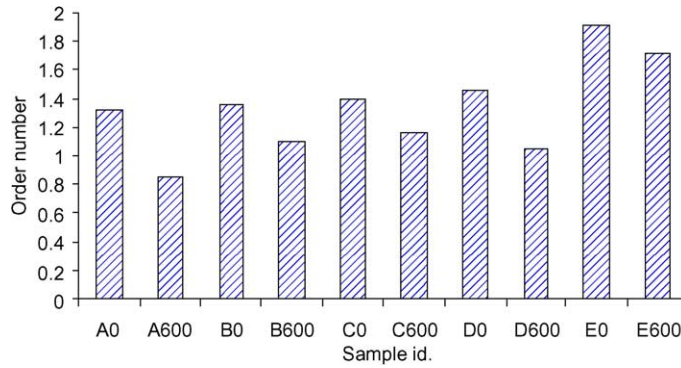
Fig. 7. Kinetic order for all samples.

4.2. Total acid number

With heating time, the color of the oil samples also changed to a darker color. This is likely due to oxidation or breakdown of color pigments. In the aspect of acid value, Fig. 8 shows the increase of TAN of the A and E oils against heating time. TAN or acid value measures the amount of acidic substances in the oil. It is defined as the amount of potassium hydroxide, in mg, necessary to neutralize the free fatty acids (FFA) in a 1 g oil sample.

Oxidation products were formed by thermo-oxidative degradation of the oil, and the oxidation occured due to the inherent unsaturated nature of the palm oil. Thermo-oxidation of the oil forms peroxides and then undergoes further reaction to form alcohols, ketones, aldehydes and carboxylic acids [15,16]. Thus, the level of the oxidation products was indicated by the level of the acid content. The relative amount of acid content was determined by titrating the oil with potassium hydroxide.
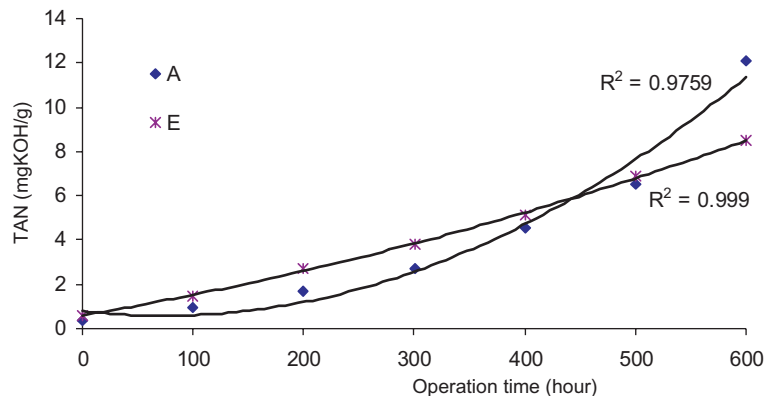

Fig. 8. Acid value for oils without additive.

The results show that the relationships between the acid value and the heating time for sample *A* are not linear but curvilinear. A second order polynomial curve fitting was used for samples *A* and *E*. It suggests that the *A* and *E* samples fit a second order polynomial with correlation coefficients for *A* and *E* as 0.9759 and 0.9990, repectively.

Although *E* has a higher acid level than *A* in the initial heating period, the *E* curve does not simulate an exponential form. On the other hand, the curve for *A* is curvilinear up, and the *A* curve crosses the *E* curve at around 450 h. At 600 h, the acid value for *A* was already 4 mg KOH/g higher than that of *E*. This shows that the *A* oil is only good to be used as a hydraulic fluid for shorter heating periods.

Fig. 9 shows the TAN traces for the *B*, *C* and *D* oils with operation time. For oils with additive, the acid value is still maintained below 2 mg KOH/g for the 600 h duration. A marginal increase of acid value was observed during 200–400 h. This occurs for all palm oil samples with additive.

The influence of additives on the production of acidic material or in depressing the acid level up to 600 h in an aerobic environment showed that the additive managed to reduce drastically the yield of acidic material. Although different additives were used, the observed trends were the same.

4.3. Viscosity

Palm oil is one of the major oils and fats in the world. This oil is attractive to be used for nonfood application from a practical point of view due to its high viscosity index. The viscosity index for palm oil was calculated as 194. Viscosity data can also be used as an indication of the oil properties during use. Fig. 10a and b show that the viscosities of *A* and *E* increased noticeably under prolonged hydraulic operation. The F10 anti-oxidant is slightly better than L135 in preventing oil thickening. Increasing the F10 amount from 1.5% to 2% offers marginal thickening depression.

4.4. Iodine value

The iodine value (IV) measures the level of unsaturated fats and oils. Fig. 11 shows that the IV for the palm oil before being degraded in the hydraulic sample as 59 cg I_2/g. This value for normal
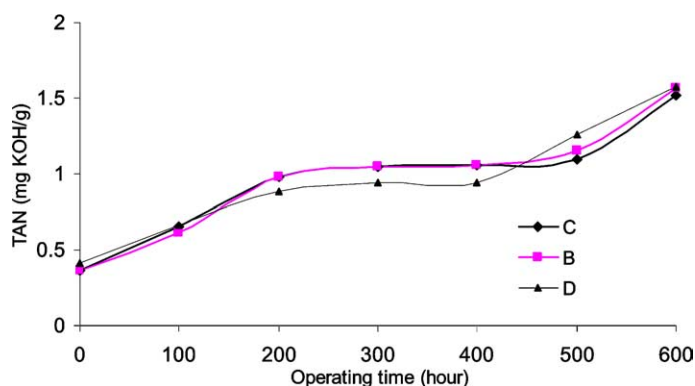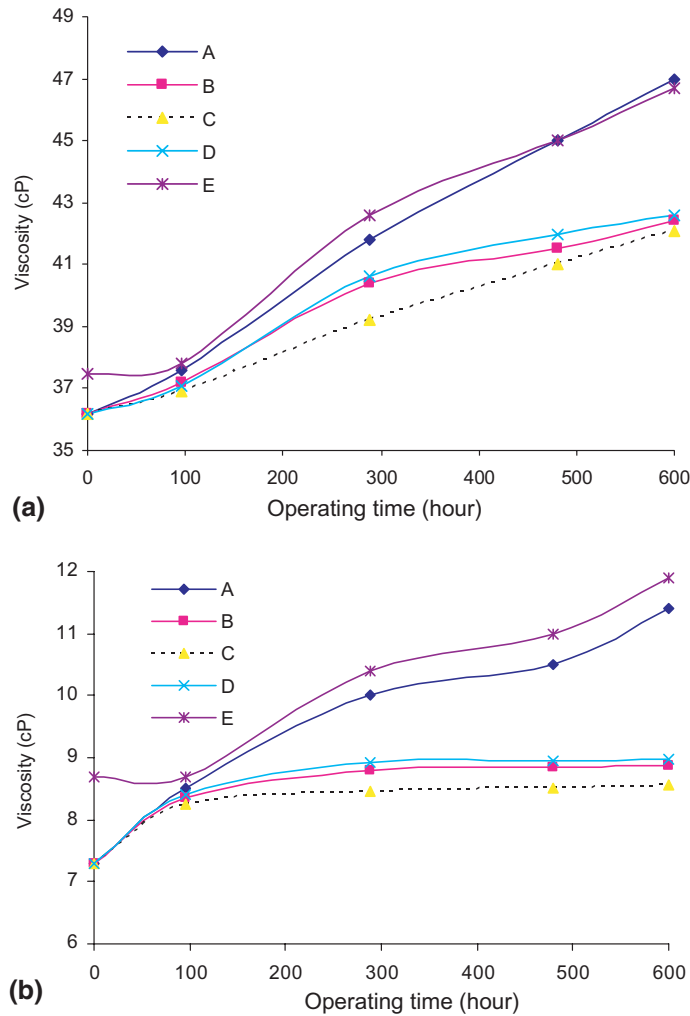

Fig. 9. Acid value for palm oil with additives.

Fig. 10. (a) Viscosity for all samples as measured at 40 °C (b) Viscosity for all samples as measured at 100 °C.

palm oil is slighly lower than that reported by Jalani et al. [17]. However, after 600 hours of heating and shearing, the IV of the palm oil without additive decreased to 43 cg I$_2$/g. This iodine value analysis indicates the decrease in the double bond of the oil sample after 600 h operation. The heating and shearing process in the hydraulic system provided energy to excite the molecules. At a certain stage, the molecules had enough energy to break the bond in the chain. Mostly, this happened to the unsaturated parts, which will then enable the saturated structure to form.

Sample E at 0 h had high IV. This is due to the high mono-unsaturated (63%) and polyunsaturated (28.4%) acids compared to sample A, which had only 43.6% mono-unsaturated and 11.8% polyunsaturated acid components. However, sample E also had undergone significant IV reduction after being heated in the hydraulic system.
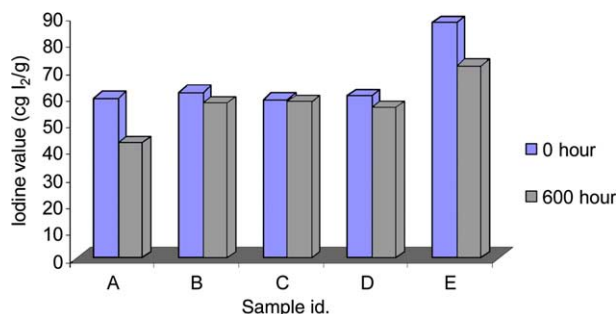
Fig. 11. Comparison of iodine values of fresh and aged oils.

The physicochemical properties of the oils after the aging test indicate that the palm oil without additive had a very high acid number increase and a relatively significant increase in viscosity. Based on acid level, the additive used has improve the thermal stability of the palm oil significantly. The use of F10 and L135 additives was found to suppress the increase of acid level and viscosity of the oil. Thus, it can be seen that the acid value, viscosity and iodine value results have similar trends as the thermal analysis results using TGA.

5. Conclusions

To date, little fundamental investigation has been made to study palm oil thermal stability. Thus, in this study, thermal degradation of palm oils and thermal stability of blended palm oils have been investigated. The effect of the anti-oxidant on thermal degradation of the oil when it was degraded in a hydraulic system at 55 °C was assessed. Besides the additive type, the additive concentration was also varied. After isothermal heating in the simple hydraulic system, the oil properties were evaluated by TGA parameters and conventional analysis using TAN, viscometric and IV indicators.

The reaction kinetics were calculated. The kinetics of the oil samples were obtained from the slopes of the mass degradation by the application of direct Arrhenius plots and integration methods. The results show that the reaction of all palm samples can be treated as a first order reaction. It seems at this stage that the additive under study can offer a significant solution in inhibiting the degradation rate of palm oil when used in a simple hydraulic circulating system. The increase in acid value and viscosity is much depressed with the introduction of the additive.

The F10 additive has a more pronounced effect on the viscosity changes than the L135 additive, while based on acid value, both F10 and L135 have equal strength. The influence of an additional amount of F10 was found to decrease the TAN value only after 500 h.

The kinetic parameters obtained from the dynamic experiments were in good agreement with conventional measurements of acid, iodine value and viscosity. Both TGA and conventional methods show that the *A* and *E* oils were not stable thermally. The methods also give similar results to the ranking of additive effectiveness. Based on TGA and conventional methods evaluation, our study suggests that F10 or L135 additive can be used in palm oil if it is going to be used as a hydraulic fluid.

Acknowledgment

We greatly acknowledge the financial support from KUSTEM (Grant No. 55002) and UTM-Ministry of Science, Technology and Environment, Malaysia (Grant No. 74033). Assistance from Mr. Azhar, Mr. Jamal, Mr. Razman and Mr. Ruzimi during the experiments is also acknowledged.

References

[1] Oommen TV, Claiborne CC. US Patent 5,949,017, Electrical transformers containing electrical insulation fluids comprising high oleic acid compositions, 1999.
[2] Demirbas A. Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: A survey. Energy Conversion and Management 2003;44(13):2093–109.
[3] Rao GAP, Mohan PR. Effect of supercharging on the performance of a DI Diesel engine with cotton seed oil. Energy Conversion and Management 2003;44(6):937–44.
[4] Demirbas A. Biodiesel from vegetable oils via transesterification in supercritical methanol. Energy Conversion and Management 2002;43(17):2349–56.
[5] Antolín G, Tinaut FV, Briceño Y, Castaño V, Pérez C, Ramírez AI. Optimisation of biodiesel production by sunflower oil transesterification. Bioresource Technology 2002;83(2):111–4.
[6] da Silva FN, Prata AS, Teixeira JR. Technical feasibility assessment of oleic sunflower methyl ester utilisation in Diesel bus engines. Energy Conversion and Management 2003;44(18):2857–78.
[7] Abdullah A, Basri MNH. Selected readings on palm oil and its uses: Malaysia. PORIM 2002:25.
[8] Wilkie CA. TGA/FTIR: An extremely useful technique for studying polymer degradation. Polymer Degradation and Stability 1999;66(3):301–6.
[9] Fornes TD, Yoon PJ, Paul DR. Polymer matrix degradation and color formation in melt processed nylon 6/clay nanocomposites. Polymer 2003;44(24):7545–56.
[10] Li XH, Meng YZ, Zhu Q, Tjong SC. Thermal decomposition characteristics of poly(propylene carbonate) using TG/IR and Py-GC/MS techniques. Polymer Degradation and Stability 2003;81(1):157–65.
[11] Torrente MC, Galán MA. Kinetics of the thermal decomposition of oil shale from Puertollano (Spain). Fuel 2001;80(3):327–34.
[12] Jaber JO, Probert SD. Non-isothermal thermogravimetry and decomposition kinetics of two Jordanian oil shales under different processing conditions. Fuel Processing Technology 2000;63(1):57–70.
[13] Pezzin APT, Duek EAR. Hydrolytic degradation of poly(para-dioxanone) films prepared by casting or phase separation. Polymer Degradation and Stability 2002;78(3):405–11.
[14] Mansaray KG, Ghaly AE. Determination of kinetic parameters of rice husks in oxygen using thermogravimetric analysis. Biomass and Bioenergy 1999;17(1):19–31.
[15] Adhvaryu A, Erhan SZ, Liu ZS, Perez JM. Oxidation kinetic studies of oils derived from unmodified and genetically modified vegetables using pressurized differential scanning calorimetry and nuclear magnetic resonance spectroscopy. Thermochimica Acta 2000;364(1–2):87–97.
[16] Shahidi F. Natural antioxidants chemistry, health effects and application. Champaign, IL: AOCS Press; 1997.
[17] Jalani BS, Cheah SC, Rajanaidu N, Darus A. Improvement of palm oil through breeding and biotechnology. JAOCS 1997;74(11):1451–5.