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Using thermal analysis techniques for identifying the flash point temperatures of some lubricant and base oils

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ABSTRACT

The flash point (FP) temperatures of some lubricant and base oils were measured according to ASTM D92 and ASTM D93. In addition, the thermal stability of the oils was studied using differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) under nitrogen atmosphere. The DSC results showed that the FP temperatures, for each oil, were found during the first decomposition step and the temperature at the peak of the first decomposition step was usually higher than FP temperatures. The TGA results indicated that the temperature at which 17.5% weigh loss take place ($T_{17.5\%}$) was nearly identical with the FP temperature ($\pm 10^\circ\text{C}$) that was measured according to ASTM D92. The deviation percentage between FP and $T_{17.5\%}$ was in the range from -0.8% to 3.6% .

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1. Introduction

Almost every lubricant used in plants today started off as just a base oil. According to the application, the final lubricant oil usually contains over 80% base oil and the remaining 20% or less is additives to enhance the performance of the base oils. The most common additives are viscosity modifiers, pour point depressant, friction modifiers, dispersant, extreme pressure, anti-wear, (and) antifoaming agent. As a result, a lubricant is a substance that reduces friction, heat, and wears when introduced as a film between solid surfaces [1,2]. Most lubricants are hydrocarbon-base fluids which can form flammable mixtures with air or other oxidizer at certain temperature and pressure conditions. Thus, the flammability characteristics of lubricating oils are useful in assessing the fire or explosion hazard which may arise during their use and storage [1–6].

Flash point temperature is defined as the lowest temperature of a liquid, corrected to 101.3 kPa, at which under specific test conditions the vapor of the sample is ignited in the presence of ignition source and the flame propagates across the surface of the sample [7]. Flash point is used as a criterion to indicate the hazard of

flammable and combustible materials. Safe conditions to transport, handle or store for flammable substances depend upon the flash point value. In principle, a high flash temperature might be preferred; however, it has been noticed that even materials with high flash points like base and lubricant oils have produced severe explosions [7–11]. Flash point can be measured using two methods: (1) open-cup (oc) method, and (2) closed-cup (cc) method [12–16]. The oc tester approximates conditions that are related in open vessels. The cc tester provides an insight into the flammability of substances within enclosed spaces such as sealed containers. Due to the large number of compounds used in industry or laboratories, it is possible to find a hazard substance without experimental flash temperature data. So, scientists around the world did not save efforts to find and develop methods to predict the flash point temperature for different types of compounds. Most of the existing methods are depending on the normal boiling point, vapor pressure, chemical structure, and heat of combustion [17–22].

Thermal analysis techniques are extremely used techniques in which a change in chemical or physical properties of a sample is measured as a function of temperature while the sample is subjected to a time controlled temperature program. In recent years, the differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) are widely used for studying the combustion behavior of fossil fuels. Besides, they are applied in studying the thermal events like melting, recrystallization, glass transitions, and decomposition of base and lubricant oils [22–30].

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The aims of this work are measuring the FP of some lubricant and base oils using Pensky-Martens closed cup (ASTM D93) and Cleveland open cup (ASTM D92) methods. Then, using DSC and TGA to identify the decomposition steps of the selected oils. After that, studying the relationship between the temperatures at certain decomposition steps and the flash point values of the selected oils.

2. Materials and methods

2.1. Materials

All oils were obtained from different companies in the Egyptian market and are coded in Table 1. The oils coded as AH1 to AH4 are lubricant oils and the oils coded as AH5 to AH12 are base oils. The viscosity of the selected oils is presented in Table 1.

2.2. Flash point measurements

The FP measurements were carried out by automatic flash point testers produced by Stanhope-Seta company, UK, according to ASTM D92 (Cleveland open cup method) and ASTM D93 (Pensky-Martens closed cup method-procedure A) [12,13]. The Cleveland open cup instrument was verified before starting measurements using FP verification solution (FP = 86.6 °C). The results obtained during verification were 87 °C. In addition, the Pensky-Martens device was verified with verification solution (FP = 198 °C) and the results obtained were 198 °C.

2.3. Differential scanning calorimeter (DSC)

DSC measurements were performed using DSC-60 instrument which was obtained from Shimadzu Company, Japan. The measurements were performed under nitrogen gas atmosphere with flow rate 300 ml/min. The samples were placed in aluminum crucibles and the samples weights were 5–6 mg. The measurements were started from ambient temperature to 500 °C and the heating rate was 5.5 °C/min for all samples.

2.4. Thermogravimetric analysis (TGA)

TGA measurements were performed using DTG-60 instrument which was obtained from Shimadzu Company, Japan. The measurements were performed under nitrogen gas atmosphere with flow rate 300 ml/min. The samples were placed in aluminum crucibles and the samples weights were 5–6 mg. The measurements were started from ambient temperature to 500 °C and the heating rate was 5.5 °C/min for all samples.

Table 1

The oils codes, producers, viscosity, FP cc and FP oc temperatures.

Oil code	Company, country	Viscosity (mm ² /s)	FP cc (°C)	FP oc (°C)	FP cc – FP oc (°C)
AH1	Mobil, Egypt	355.14	206	244	–38
AH2	Shell, Egypt	387.7	218	255	–37
AH3	Total, Egypt	356.9	222	267	–45
AH4	Rheinol, Germany	200.17	198	244	–46
AH5	APRC – Ameria petroleum Refining Co., Egypt	30.65	202	230	–28
AH6	APRC – Ameria petroleum Refining Co., Egypt	32.78	200	222	–22
AH7	APRC – Ameria petroleum Refining Co., Egypt	51.35	220	244	–24
AH8	APRC – Ameria petroleum Refining Co., Egypt	13.88	186	202	–16
AH9	APRC – Ameria petroleum Refining Co., Egypt	229.01	230	272	–42
AH10	APRC – Ameria petroleum Refining Co., Egypt	14.44	188	192	–4
AH11	APRC – Ameria petroleum Refining Co., Egypt	62.82	220	240	–20
AH12	APRC – Ameria petroleum Refining Co., Egypt	14.37	184	192	–8

3. Results and discussion

3.1. Flash point of base and lubricant oils

The results of FP cc and FP oc temperatures for lubricant and base oils are presented in Table 1. It is clearly seen in Table 1 that the FP temperatures in cc tester for lubricant and base oils are ranging from 184 °C to 230 °C while in oc tester the results are extending from 192 °C to 272 °C. The oc results are always higher than cc results. Except AH10 and AH12 samples, the difference between cc and oc values, for the same oil, is higher than 15 °C and lower than or equal to 46 °C. The higher oc values are referred to that during the test some of the flammable volatile products leave the cup surface, where the ignition source is applied, to the surroundings. As a result a temperature higher than FP temperature in cc method is required in order to produce the flammable vapors above sample surface in concentrations sufficient to ignition after application of an ignition source. In contrast, the cc method provides relatively lower values of FP, because the closed system prevents the escape of volatile products and approximates equilibrium between vapor and the air in the enclosed space. The flammable vapors in cc method are trapped and concentrated in closed system and this help in reaching the flash point temperature earlier than oc test method [22,31].

3.2. DSC of lubricant and base oils

Fig. 1 shows the DSC curves of lubricant oils. It is evident that the lubricant oils can have more than one decomposition step

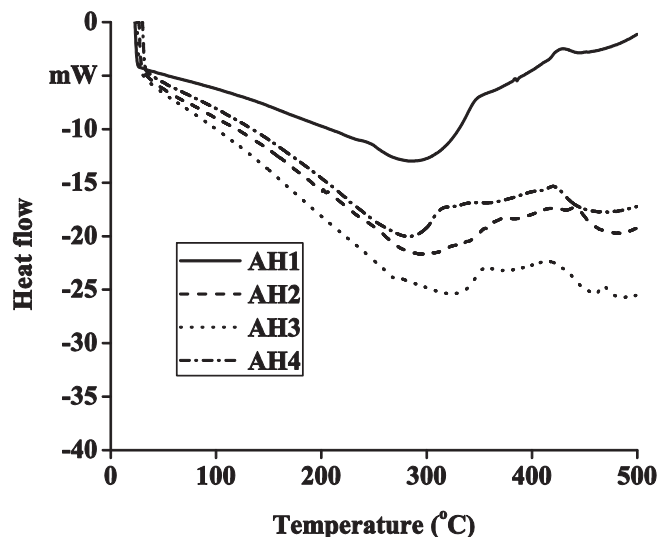


Fig. 1. DSC curves for lubricant oils.

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