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# Influence of antioxidant on the thermal–oxidative degradation behavior and oxidation stability of synthetic ester

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ABSTRACT

The influence of pentaerythritol tetrakys 3-(3,5-ditert-butyl-4-hydroxyphenyl) propionate (1010) and octylated/butylated diphenylamine (L57) on the thermal–oxidative degradation of di-2-ethylhexyl sebacate (DEHS) was studied by using model-free thermo analysis under air atmosphere. Activation energies about the thermal–oxidative degradation of lubricants were evaluated by Kissinger–Akahira–Sunose (KAS) method. Pressure drop test (PDT) and pressurized differential scanning calorimetry (PDSC) tests were also employed to study their antioxidant performance in DEHS. The results showed that the addition of 1010 and L57 could enhance the oxidation stability of DEHS and increase the activation energy of thermal–oxidative degradation especially at the initial stage of thermal–oxidative decomposition. Meanwhile, a good corresponding relationship was found between model-free method and traditional test methods.

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## 1. Introduction

Thermal–oxidative degradation has been a persistent problem for lubricants, in particular for those synthetic esters mainly applied in industrial and engine oil, due to their high-temperature working conditions [1–4]. Many harmful oxidation products are formed during this process, and they always bring a lot of unfavorable influences to the lubricant system [5,6]. Many researchers have tried to enhance the oxidation stability of lubricants by introducing antioxidants into the lubricant system to restrain the oxidative degradation of oils [7–9]. Phenol-type antioxidants and amine-based antioxidants are the most important classes of antioxidants being extensively used for their good performance in protecting the lubricants from oxidative degradation as well as guaranteeing the oils to properly meet the requirements of the industry [10,11]. Also a series of methods have been reported to evaluate the antioxidant performance of antioxidants as well as the oxidative behavior of lubricants including hot oil oxidation test (HOOT), rotary bomb oxidation test (RBOT), thermogravimetric analysis (TGA), differential thermal analysis (DTA), pressurized differential scanning calorimetry (PDSC), differential scanning calorimetry (DSC), etc. [12–14]. Nevertheless, the kinetics aspects of the thermal–oxidative degradation of lubricants with and without antioxidants have never been reported in the current literature.

As previously mentioned, the thermal–oxidative degradation of lubricants is a very complex process comprising many chain reactions, which are difficult to analyze separately and whose quantitative contribution to the global degradation process is virtually impossible to assess. Moreover, the addition of antioxidants to lubricants can affect the oxidative behavior of the whole lubricant system, so it is of great significance to obtain the kinetic information about the thermal–oxidative degradation of lubricants with and without antioxidants to know how antioxidants affect the thermal–oxidative degradation of lubricants at different oxidation stages.

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) have been widely used to estimate the kinetic parameters of thermal degradation and oxidative degradation processes, such as activation energy ($E$), reaction orders ($n$), and the Arrhenius pre-exponential factor ($A$) [15–20]. In general, model-fitting and model-free methods are the most used approaches to analyze the kinetic data from TGA and DTG. Model fitting methods always use different models to choose a model that can provide the best statistical approximation during the calculation of the kinetic parameters [21]. While for model-free methods, several kinetic curves are required to perform the analysis. The data from several curves with different heating rates on the same value of conversion are used to calculate the activation energy for each conversion point [22–24]. Compared with model-fitting

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methods, model-free methods are more recognized for their simplicity and avoidance of errors connected with the choice of a kinetic model. In all the model-free methods, Kissinger–Akahira–Sunose (KAS) method is the typical representative of good correlation and accuracy [25,26]

In this paper, the influence of 1010 and L57 on the thermal–oxidative degradation behavior of DEHS was analyzed by Kissinger–Akahira–Sunose (KAS) method which could give the kinetic information about the thermal–oxidative degradation of lubricants. For a comparison purpose, PDT and PDSC tests were also used to study their antioxidant performance in DEHS.

This study can contribute to getting knowledge of the thermal behavior of lubricants under real atmosphere and further knowing how the antioxidants affect the thermal–oxidative degradation of lubricants at different oxidation stages. In addition, this work also provides a new method for quick and exact estimation the anti-oxidation stability of antioxidants and is help to extend life expectancy of lubricants.

## 2. Experimental

### 2.1. Materials

The base oil used in this work was DEHS, a kind of synthetic ester oil supplied by Sinopharm Chemical Reagent Co. Ltd. (China). The antioxidant 1010 was obtained from Shandong Linyi Sunny Wealth Chemicals Co. Ltd. (China). The antioxidant L57 was purchased from Ciba Company. Their molecular structures are shown in Fig. 1.

### 2.2. Methods and apparatus

The procedure of mixing the antioxidants with the base oil is shown as following: antioxidant (1 wt%) was added to base oil (99 wt%) at room temperature, then the mixture was mechanically stirred at 60 °C for 30 min. Thus, the base oil with antioxidant was clear and transparent.

The thermal properties of DEHS and DEHS with antioxidants were investigated by thermogravimetric analysis (TGA) performed on NETZSCH STA 449C instrument (Bavarian, Germany). They were heated from 25 to 600 °C in air atmosphere with the heating rates of 10, 15, 20, 40 °C/min respectively.

PDT tests were carried out on the SYD-0193 equipment (Shanghai Changji Instruments Co. Ltd. China). The bomb with 50 g sample was charged with oxygen to 500 kPa at room temperature, and then it was held for 1 h at 150 °C and timing started. The pressure of test oils was recorded for 24 h interval, and this process lasted for 120 h.

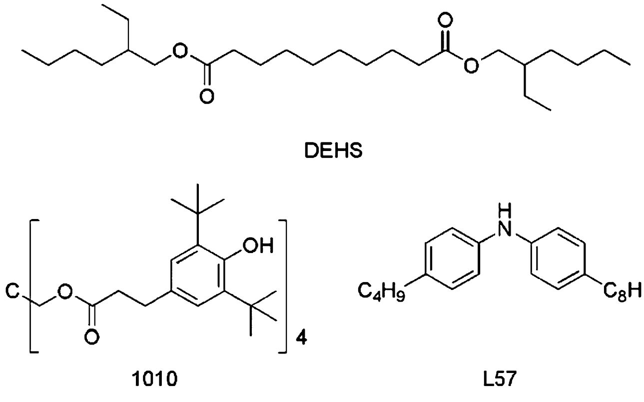

Fig. 1. The chemical structures of the selected materials.

PDSC experiments were carried out using NETZSCH DSC 204HP instrument (Bavarian, Germany). The oxygen flow rate was 100 mL/min and the pressure of high-purity nitrogen was 3.5 MPa. Temperature programmed experiments were heated from ambient temperature to 350 °C with a heating rate of 10 °C/min. The initial oxidative temperature (IOT) could be obtained through temperature programmed experiment.

### 2.3. Kinetic theory

According to non-isothermal kinetic theory, the decomposition rate can be described by following equation [26]:

$$\frac{d\alpha}{dT} = \frac{A\exp(-E/RT)}{\beta} f(\alpha) \qquad (1)$$

where $\alpha$ is the extent of conversion, $T$ is the absolute temperature (K), $A$ is the Arrhenius pre-exponential factor ($s^{-1}$), $E$ is the apparent activation energy (kJ/mol), $R$ is the gas constant (J/mol/K), $\beta$ is the heating rate (K/min).

Activation energy ($E$) is the most important kinetic parameter for obtaining the kinetic information about the thermal–oxidative degradation of lubricants. In this study, we selected Kissinger–Akahira–Sunose (KAS) method to calculate the activation energy (E) of DEHS with and without antioxidant according to the suggestions from ICTAC Kinetics Committee.

Kissinger–Akahira–Sunose (KAS) method is a differential method allowing the evaluation of Arrhenius parameters, which has the advantage that does not need the knowledge of the exact thermo-degradation mechanism. The $E$ can be obtained through the following equation [26–29]:

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

The activation energy at fixed $\alpha$ can be calculated by plotting a curve of $\ln(\beta/T^2)$ vs. $1/T$, which should result in a straight line with a slope equal to $-E/R$.

## 3. Results and discussion

### 3.1. Thermal stability of DEHS and DEHS with antioxidants

The addition of antioxidants can restrain the oxidative process of lubricants and reduce the generation of oxidative products which are always with low weight and easily to evaporate or decompose at elevated temperature. In other words, the addition of antioxidants has great influence on the thermal stability of lubricants. Fig. 2(a–c) illustrates the TGA and DTG curves of DEHS and DEHS with 1 wt% antioxidants at different heating rates (10, 15, 20, 40 °C/min) in air atmosphere. All the TGA profiles show similar trends, indicating the homologous thermal–oxidative degradation of DEHS and DEHS with antioxidants. The onset decomposition temperature ($T_{onset}$) which is used to indicate the resistance of the oils to thermal–oxidative degradation is designated as the intersection of the extrapolated baseline and the tangent line of the curve with maximum slope (TGA curve). The maximum degradation temperature ($T_{max}$) is defined as the degradation temperature corresponding to the maximum weight loss rate (DTG curve). Table 1 shows the results of $T_{onset}$ and $T_{max}$ of all samples at different heating rates. It can be observed from the TGA curves that the curves shift toward higher temperatures as the heating rate increases for DEHS and DEHS with 1 wt% antioxidants. The onset temperatures of all the samples also increase with the increase in heating rate. This can be attributed to the fact that the sample spends a longer time at a certain temperature with lower heating rates, in other words, with a longer residence time at that

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