

Kinetic studies on thermal degradation of automotive lubricant oils and estimation soot content by TGA

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دراسة حركية الأنحلال الحراري لزيوت تزييت المحركات وتقدير محتوى السناج بواسطة التحليل الحراري الوزني

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المستخلص

تم توصيف التفكك الحراري لزيوت التزييت بتقنية التحليل الوزني الحراري TGA ضمن محيط خامل من غاز الهليوم عند معدلات تسخين 5, 10, 20, 30, 40 درجة مئوية / دقيقة اعتمادا على فقدان الوزن كدالة لدرجة الحرارة. للحصول على المتغيرات الحركية الكيميائية ووصف عملية التفكك تم تحليل منحنيات التحليل الوزني الحراري TGA مع منحنيات التفاضل باستخدام طريقة Coast-Redfern. النتائج كانت مرضية وتوصف العلاقة الخطية وبدقة قريبة جدا من الواحد باستخدام برنامج SPSS الحزمة الأحصائية وكانت النتائج متوافقة مع القيم المنشورة. وتضمنت الدراسة الحالية وصف طريقة تحديد كمية الكربون بما يدعى Soot للزيوت المستخدمة. الدراسة تهدف وصف عملية التفكك الحراري وعلاقتها بمتغيرات الحركية الكيميائية والخواص الثرموديناميكية وقياس كمية السناج أو الكربون المتفحم.

Abstract

Thermal degradation of fresh automotive lubricant characterized using TGA technique under Helium atmosphere at different heating rate 5, 10, 20, 30, 40 C° /min based on mass loss as a function of temperature. To obtain the kinetic parameters and to describe the thermal decomposition of lubricant, TGA curves and their derivatives were analyses using Coast-Redfern methods. Kinetic parameters were determined was satisfactory presenting good correlation with linear correlation coefficient close to unit using SPSS package and was in a good agreement with publishes data. Also the present study describes soot content determination for different used lubricant. This wok aims to characterize the thermal decomposition process in relation to its kinetic, thermodynamic property and measure amount of soot.

Introduction

Lubricant oils are highly sophisticated blend of hydrocarbons and additives. They are used in diesel and gasoline engines. The oil is exposed to high thermal stress which affects the oil properties due to combustion, evaporation of volatiles or thermal degradation and polymerization to form heavier fraction. These processes may lead to a higher viscosity of the oil. Incomplete combustion of fuels results in the formation of soot. Sooting is believed to be

a major cause of engine wear, and soot if left unchecked will become a residue that will clog the internal parts of diesel and gasoline engines. Therefore it is vital to perform regular oil analysis to ensure good oil quality and low soot content. To evaluate lubricant oils the thermo gravimetric analysis (TGA and DTG) is considered to be a more accurate technique for soot content determination and study the thermal degradation kinetics has been widely accepted among researchers leading to meaningful economy (1-10). At temperatures greatly exceeding the thermal stability point of the lubricant, larger molecules will break apart into smaller molecules. This thermal cracking, often referred to as thermal breakdown can initiate side reactions, induce polymerization, produce gaseous by-products, destroy additives and generate insoluble by-products. In some cases, thermal degradation will cause a decrease in viscosity. The degradation energy and thermal stability can be evaluated by kinetic and thermodynamic study (1).

Experimental

Mineral lubricating oil produced by Jumbo Oils was used in this study. Different samples were withdrawn at different time from gasoline engine after performance. The thermo gravimetric measurements were carried out by a Perkin Elmer TGA analyzer, in non-isothermal condition. These experiments were carried out at Ibin Sina company (Ministry of Industry). The fresh samples weight was (51.1, 29.0, 26.2, and 18.6 mg). Decomposition profiles were obtained while heating rates at 5, 10, 20, 30, and 40 C°/min in Helium atmosphere with a flow rate of 20 ml/min between 30-600C° as well as four used sample at different distance in modern gasoline engine to evaluate the amount of soot content by subjecting it to high temperature with heating rate 20 C°/min by TGA, and estimate the residual deposit from dynamic TGA curves, these experiment performed according ASTM D5967 (11). The sample mass was heated in a standard ceramic pan.

Results and discussion

Sooting

Soot is composed of a number of chemical components resulting from incomplete fuel combustion (gasoline, diesel, bunker, kerosene). It was presented in the form of dark, carbon-rich tar-like solid substances called carbon soot or black carbon. The presence of soot in oil is totally normal given a certain number of kilometers or hours of operation. When not exhausted into the atmosphere through the exhaust system, soot is absorbed by the lubricant. Fig.1 shows the measured percentage soot as function of time by using TG analysis for different level of soot. However, it can be seen that soot increases with distance of using oil in gasoline engine. However the data are in agreement with published data (12).

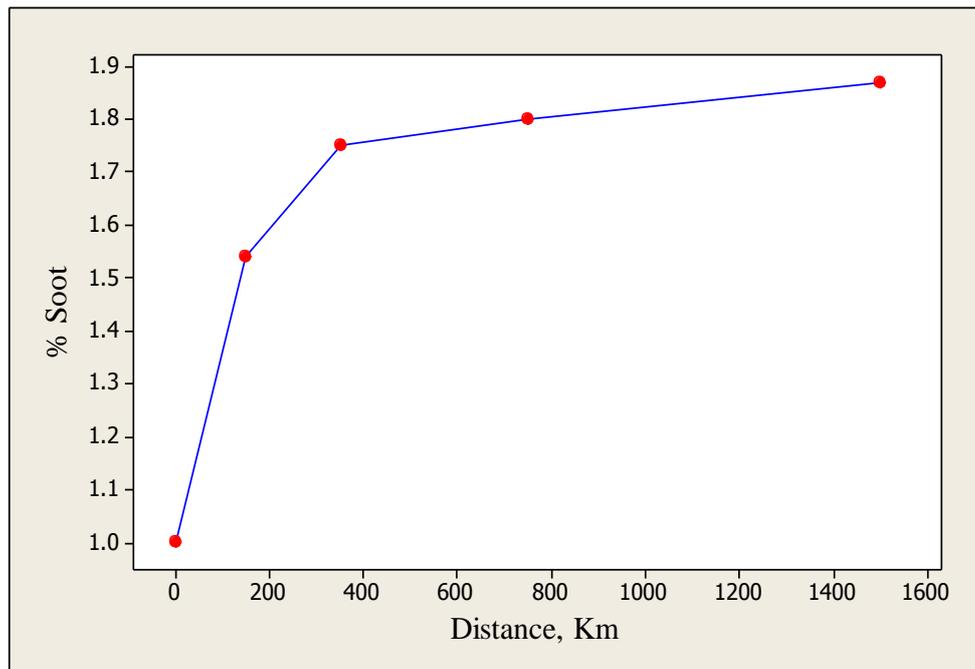


Figure (1): Effect of distance on soot content

Thermogravimetric analysis (TGA)

The typical TGA and DTG are shown in Figure 2. It shows the data of weight loss versus degradation temperature. It can be seen that the lubricant sample degraded between 200 C^o and 450 C^o loss in volatility followed by thermal decomposition of lubricant resulting higher molecular weight finally products 0.08wt% deposit for fresh lubricating oil. Fig 3 shows TGA curves obtained at heating rate of 5, 10,20,30,40 C/min representing residual mass versus temperature. It can be seen not only the volatility only parameter that can be directly linked to lubricant consumption as mentioned by Gustavsson ,1991 (13) and Perez ,2000 (14) who mentioned the deposit besides volatility during oxidative decomposition of lubricating oil.

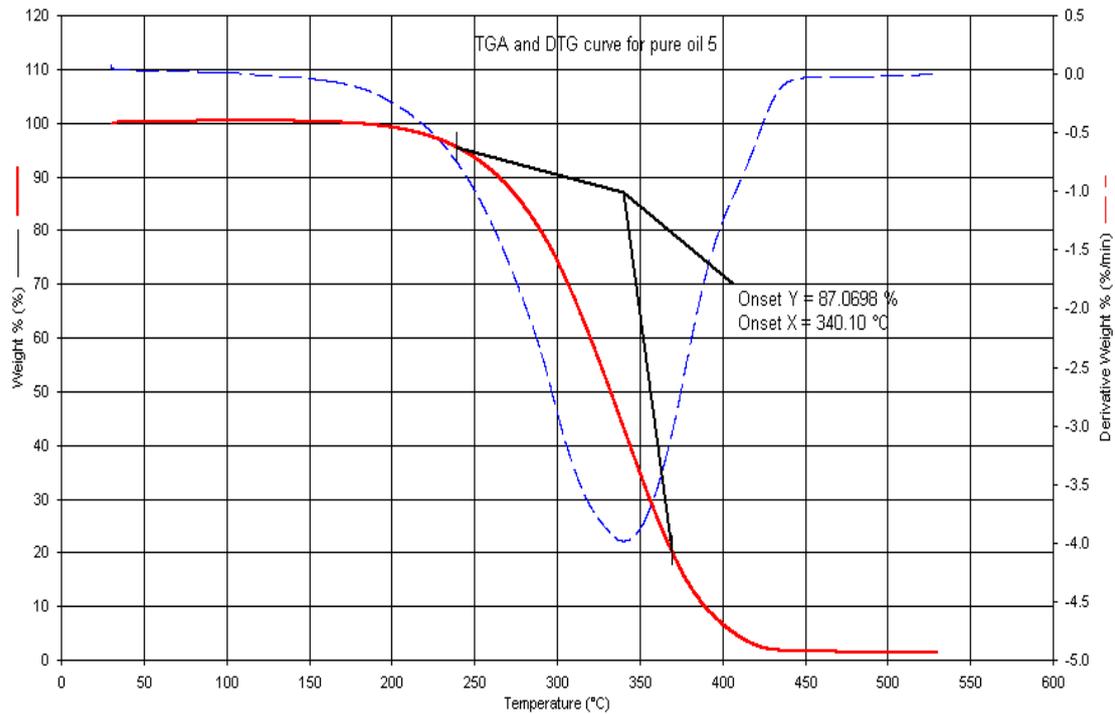


Figure (2):TGA and DTG curve recorded under Helium atmosphere at $\beta = 5 \text{ C}^{\circ}/\text{min}$

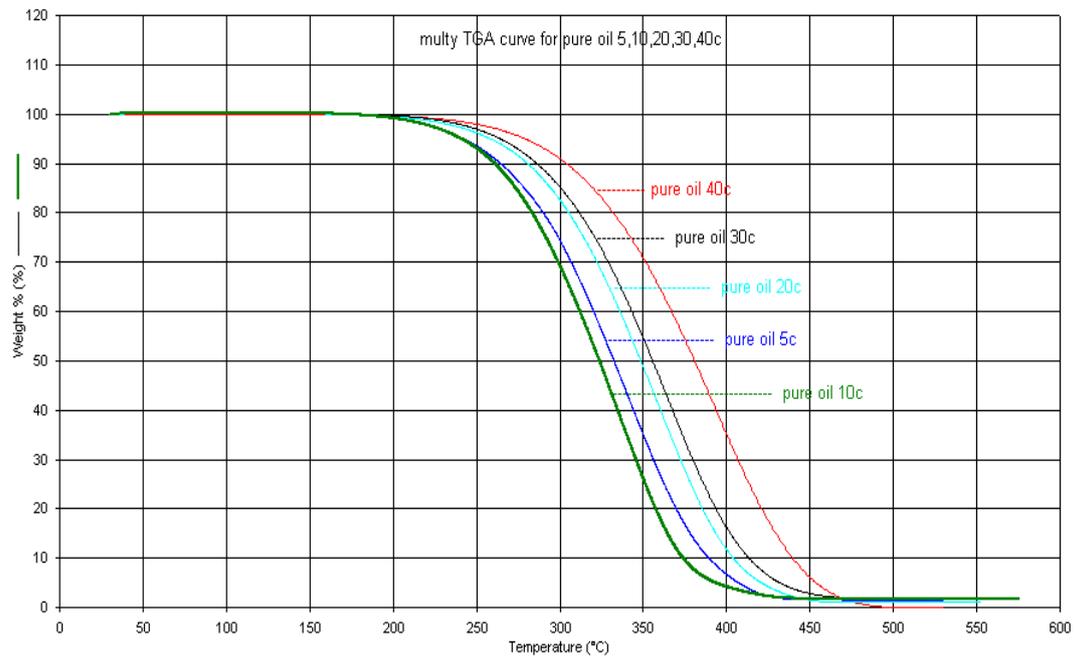


Figure (3): TGA curves recorded under Helium atmosphere at various β

The data as shown in Table 1 were manipulated to get corresponding data needed to the plot in Fig 4 at different heating rate by utilizing Coast-Redfern method, which can apply to TGA data for different reaction order. Solid lines represent the best fit of experimental data by

using SPSS package with high accuracy R^2 were activation energy, E and frequency factors, A_0 and reaction order may be easily calculated.

Table (1): Numerical data of thermal degradation at different level of β

(1- α)	T ,K $\beta =5$ C°/min	T ,K $\beta =10$ C°/min	T ,K $\beta =20$ C°/min	T ,K $\beta =30$ C°/min	T ,K $\beta =40$ C°/min
0.1	643.8	664.9	683.0	689.25	712.0
0.2	628.2	643.8	655.8	668.0	693.0
0.3	618.8	629.5	643.8	653.0	678.0
0.4	608.4	618.8	632.1	638.0	665.5
0.5	595.4	605.8	618.8	628.0	653.0
0.6	584.7	595.1	605.8	615.5	638.0
0.7	573.0	578.0	592.5	601.7	623.0
0.8	558.4	563.6	575.6	585.5	603.0
0.9	534.7	541.2	551.9	560.5	575.0

The Coast-Redfern (15) ^{method} is multi-heating rate application Coast-Redfern equation. The formula for first order reaction ($n=1.0$) :

$$\ln\{-\ln(1-\alpha)/T^2\} = \ln(A_0R/\beta E)\{1-(2RT/E)\}-(E/RT) \quad (1)$$

For $n \neq 1.0$

$$\ln\{[1-\ln(1-\alpha)]^{1-n} / [T^2(1-n)]\} = \ln(A_0R/\beta E)\{1-(2RT/E)\}-(E/RT) \quad (2)$$

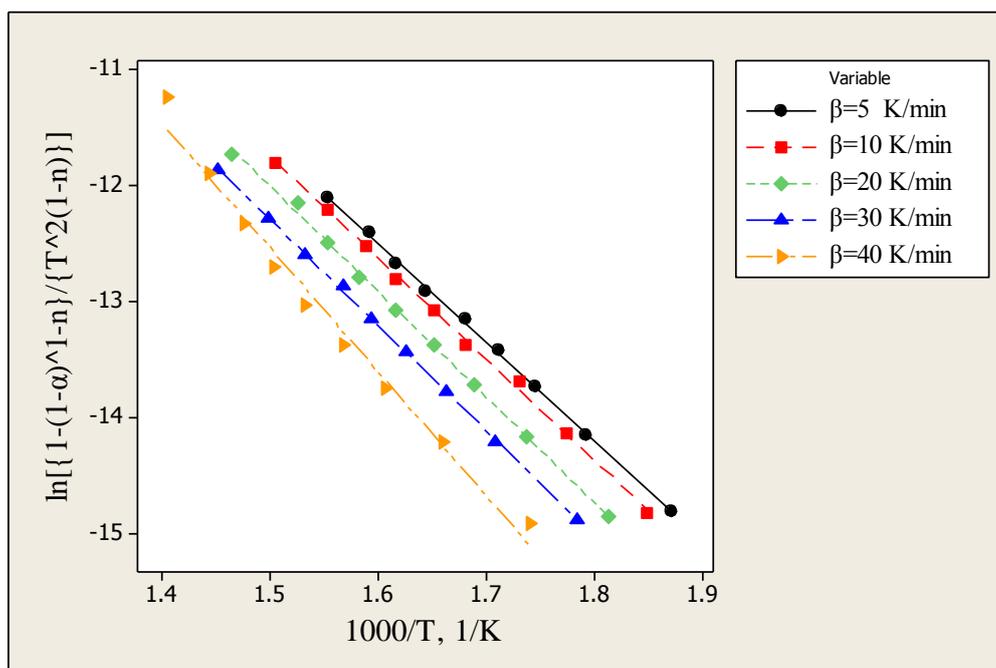
Thus plot for $n=1.0$

$\ln\{-\ln(1-\alpha)/T^2\}$ against $1/T$ for each heating rate gives a family of straight lines of slope $-E/R$.

or plot for $n \neq 1.0$

$\ln\{[1-\ln(1-\alpha)]^{1-n} / [T^2(1-n)]\}$ against $1/T$ for each heating rate gives a family of straight lines of slope $-E/R$.

The data of weight loss versus degradation temperature completed by TGA were manipulated to get corresponding data needed to the plot in Fig.4 at different heating rate. However solid line represent the best fit of experimental data by using SPSS computer package were activation energy, E, frequency factors, A_0 , and reaction order may be easily calculated as shown in Table 2 these results are in a good agreement with published data (1,2).

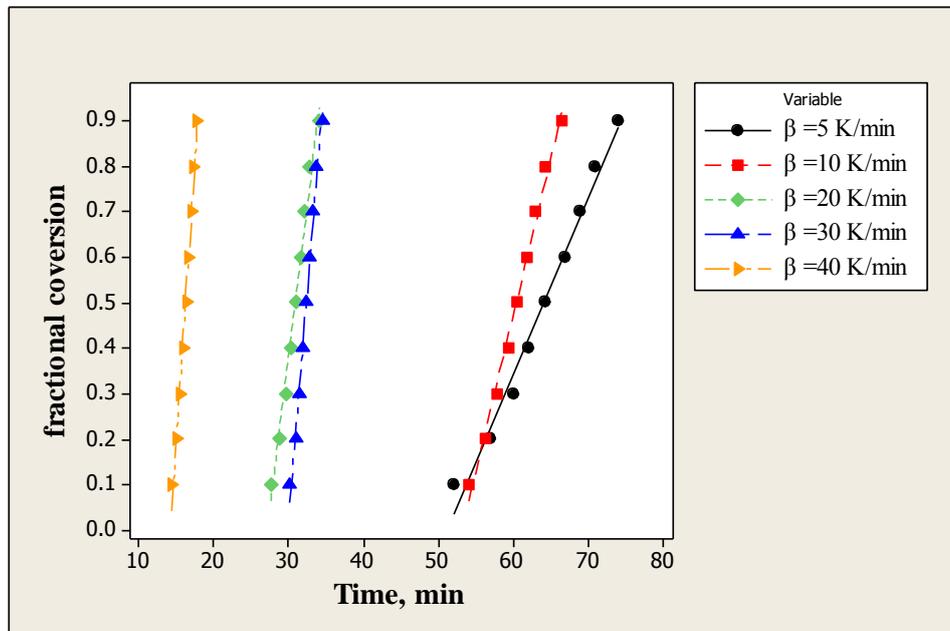


Figure(4): Coast-Redfern plot for thermal degradation at different β

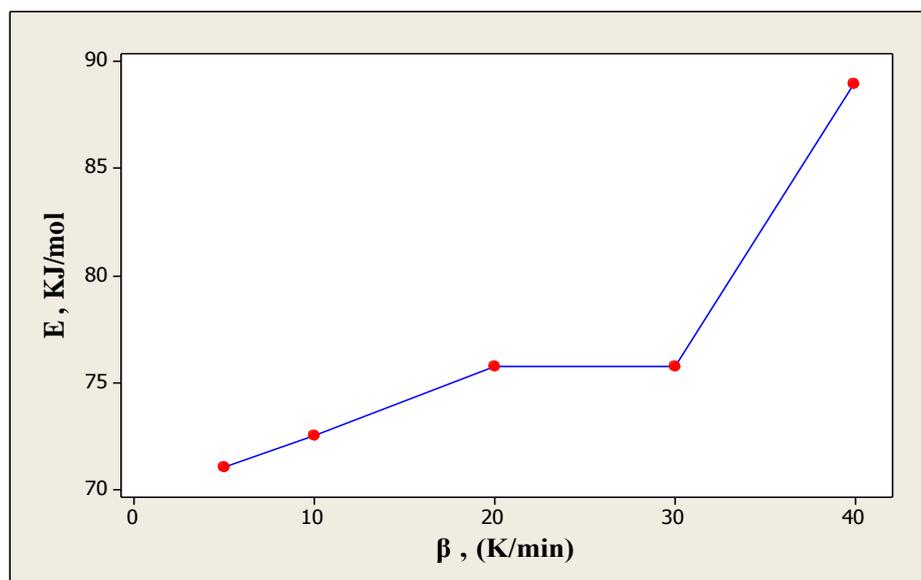
Table (2): Influence of heating rate on kinetic parameter of lubricant oil

Heat rate β (C°/min)	T_{peak} ,(K)	Reaction order, n	Activation energy, E (kJ/mol)	Factor, A_0 (S ⁻¹)	R ²
5.0	607.7	1.0	71.052	2.6850×10^3	0.999
10	613.1	1.3	72.516	6.3636×10^3	0.999
20	630.2	1.4	75.732	1.8367×10^4	0.999
30	631.7	1.3	75.748	2.0710×10^4	1.000
40	653.5	1.8	88.986	27.1710×10^4	0.992

Fig.5 showed the effect of heating rate on thermal decomposition of lubricant oil; however fraction of decomposed oil increases with increasing of heating rate. It can be seen more ingredient of oil lubricant volatilized as well as increasing the values of kinetic parameters. However it can be seen at high temperature the activation energy increases due to the formation of intermediate higher molecular weight compound resulting of the decomposition. The substance formed in the degradation process by TGA are hydrocarbons and ester presenting a high molecular weight besides more stability which needs higher energy values to decompose(16) as shown in the Fig.6 .



Figure(5): Effect of heating rate on thermal decomposition of lubricant



Figure(6): Effect of heating rate, β on activation energy

The thermodynamic properties were determined by the following equations (17,18):

$$\Delta H = E - R T_{\text{peak}} \quad (3)$$

$$\Delta S = R [\ln(h A_o / k_b T_{\text{peak}}) - 1] \quad (4)$$

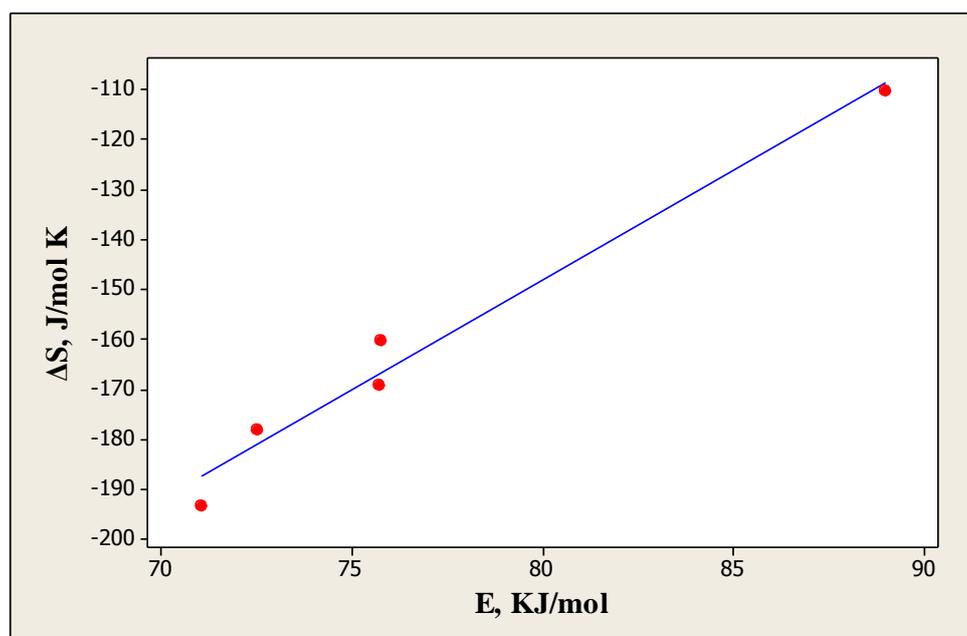
$$\Delta G = \Delta H - T_{\text{peak}} \Delta S \quad (5)$$

Where ΔH is activation enthalpy, ΔS is activation entropy, ΔG is activation free energy, T_{peak} is maximum peak temperature, h is Plank constant and k_b is Boltzmann constant. Table 3 shows the thermodynamics property of fresh degraded lubricant oil.

Table (3): Influence of heating rate on thermodynamic parameters

Heat rate β (C°/min)	T_{peak} ,(K)	ΔH ,KJ/Kmol	$-\Delta S$, J/Kmol	ΔG , KJ/Kmol	R^2
5.0	607.7	65.999	193.500	183.579	0.999
10	613.1	67.418	178.082	176.549	0.999
20	630.2	70.493	169.366	177.185	0.999
30	631.7	70.496	160.210	184.756	1.000
40	653.5	83.552	110.038	155.437	0.992

Fig. 7 showed the relationship between values of activation energy, E and Entropy, ΔS clearly shows a good linear relationship between them with accuracy $R^2=0.976$ as it has been investigated by several workers (19,21). The existence of the same linear dependence between activation energy and entropy, however that is a compensation effect and can be interpreted as a proof that the mechanistic kinetic equations employed adequately reflect the specific kinetic parameters characterizing these process were correctly calculated. On the other hand the existence of linear relationship between activation energy and entropy provide a solid basis for seeking directly relationship between them, that is the value of activation energy of similar decomposition process exert a certain effect of value of the change in entropy.



Figure(7): Plot of ΔS against E for thermal decomposition of the lubricant

Conclusion

The decomposition kinetics, thermodynamic properties and soot of lubricant investigated using TGA under inert atmosphere. When lubricant oil is heated beyond a certain temperature, it will start to degrade even if there is no oxygen present. The TGA data obtained from dynamic measurement showed that the lubricant degraded between(200-450). Kinetic and thermodynamic parameters verified that the reaction mechanism of lubricant oil changed significantly. The activation energy was determined for different heating rate with the help of Coast-Redfern, and it was good agreement with published data. Therefore it can be concluded that TGA are a useful tools for investigating thermal stability and provide accurate way to soot measurement.

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