



Thermal Decomposition of Lubricating Oil Under an Inert Atmosphere

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(Received: 24 May 2010;

Accepted: 7 February 2011)

AJC-9594

Weight losses in the thermal degradation of SAE 40 oil have been studied by means of dynamic experiments, carried out under nitrogen atmosphere. At slow heating rates the thermal decomposition phenomenon becomes very lucid. Furthermore, oil in use becomes thermally unstable and loses progressively its initial lubricant power also volatile organic fraction become affected by the ageing when the number of working hours of engine is increasing.

Key Words: Diesel engine marine, Lubricating oil, Thermogravimetric analysis, Pyrolysis, Heating rate effect.

INTRODUCTION

Thermoanalytical methods such as thermogravimetry (TG) have been used extensively in studies related to energetic material, especially regarding the degradation of different material. The advantages of the thermogravimetric methods are their speed, precision and reproducibility of weight loss determination. Also, the temperature information and the rate of degradation are used to identify or characterize materials.

The rate of weight loss of material by thermal decomposition is strongly influenced by the experimental conditions such as heating rate, flow gas, physical and chemical characteristics of the material in question¹⁻⁴.

In the present work, some new results are presented for pyrolysis process of SAE 40 oil. This is followed by a description of thermogravimetry (TG) and derivative thermogravimetry (DTG). The aim of study is to attempt to predict the overall behaviour of this oil.

EXPERIMENTAL

Thermogravimetric measurements were performed using a Mac Bain and Baker thermobalance made in the laboratory by Prof. L. Belkbir. The principal components of the balance are a spring and a reaction tube of quartz inside of which is the sample holder which is suspended from the bottom of the spring. The change in sample weight causes stretching and contraction of the spring. These variations in spring length are followed by a micrometric telescope. The experimental temperature is provided by a tubular furnace. The thermo-

couple head is located in the reaction tube to reduce the temperature gap between the sample and the tube⁵. This remarkably affects the isothermal and non-isothermal kinetics results of the decomposition of the material in question.

Present study consists to follow the thermal degradation of oil lubricating a four-stroke marine diesel engine having a power of 2200 horse-power and the degradation of the oil of lubrication by thermogravimetric analysis (TGA). The oil in question has a class SAE 40 based on highly-refined mineral oil naturally paraffin specially designed for main propulsion and auxiliary marine trunk piston engines burning distillate fuel.

Along 1000 WHE (working hours of engine) and at each 100 WHE in normal navigation after complete oil drain of the crankcase of present engine adding up 3805 WHE. The oil samples are taken by drainage before its return to the crankcase of the engine in working.

The weight losses for SAE 40 oil were measured in an inert atmosphere. The thermal decomposition of each sample was studied separately. All the experiments were carried out under the same operating conditions.

RESULTS AND DISCUSSION

New oil pyrolysis: We achieved a slow pyrolysis of 5 mg of new oil (0 WHE) since the ambient until a final temperature $T_f = 620$ °C using a heating rate of 15 °C min^{-1} under a nitrogen flow of 20 mL min^{-1} . Typical thermograms were shown in Fig. 1 which represents the TG and DTG curves of new oil in inert atmosphere.

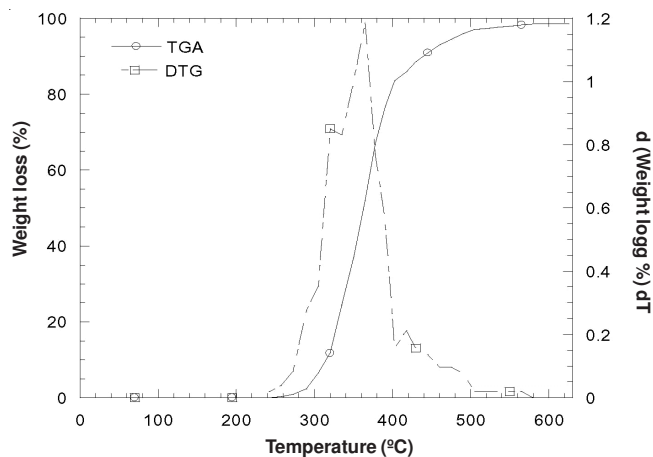


Fig. 1. TGA and DTG curves of new oil pyrolysis

It is noticed that the thermal decomposition of the oil begins slowly to surroundings of 240 °C. We can affirm that were lube oil have a good thermal stability. Indeed, for normal oil the clearing of the volatile organic fraction⁶ (VOF) generally begin beyond of 150 °C. Besides, we can consider that all paraffinic oil clearing VOF above 200 °C is thermally steady⁷. This thermal stability provide to the lubricating oil a good resistance to the very stern thermal conditions of diesel engine and a preservation of the chemical structure for a long useful life.

Between 240 and 320 °C, we observe a small fluctuation of the thermogram indicating a weak loss of mass (12 %) justified by the lightest VOF departure. Indeed, when we heat a polymeric material the lateral groups begin to vibrate^{1,8}. In addition to these vibrations and following the energy brought by the increase of temperature, movements of rotation occur. When the contribution of energy is sufficient, the lateral groups begin to detach themselves of the main structure following their strengths of bonding^{1,8}.

The analysis of the DTG curve shows that the VOF contains several families of organic matter. Between 320 and 400 °C the loss becomes more fast (70 %), which is attributable to the departure of macromolecules resulting to cracking of the main chain. Above 400 °C, the thermogram tilts by effect of the slowing of the thermal degradation phenomenon and becomes practically parallel to the abscissas axis. This phenomenon can be explained by the macromolecules polycondensation¹ which form the solid residual having crystalline form and presenting 1.47 % of the initial weight of sample (Soot and additives residual). According to Buhaug⁹ and Miyazaki *et al.*¹⁰ the significant inorganic fraction fixed by diesel engine piston and cylinder liner (hot side of engine) is freed by the additives.

Lubricant oil samples pyrolysis: We proceeded to the slow pyrolysis from the ambient temperature to 620 °C of all

lubricating oil samples (0, 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 WHE) with the same operating conditions. Fig. 2 presents the pyrolysis thermograms of all the samples.

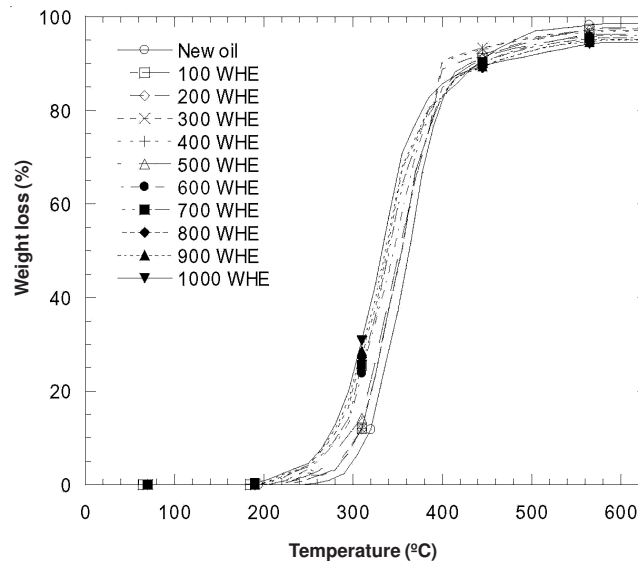


Fig. 2. TGA curves of all oil samples pyrolysis

The tracings indicate that the temperature of thermal decomposition onset of different samples has a decreasing evolution as a function of the working hours of present diesel engine (Table-1). This decreasing evolution explains a progressive loss of the initial thermal stability of oil in the new state.

Following the number of working hours of engine, thermograms move toward the weak temperatures. Indeed, oil loses progressively the thermal stability¹¹. Besides following the wear of contact surfaces of the engine the oil in use contains more wear metallic particles. These two phenomena lead to a thermal degradation of oil. Metallic particles have a selective action which explains the position and the progression of thermograms as well as the solid residual rate. This rate undergoes a logical following according to the working hours of engine (Table-1). This result corresponds to the one gotten by spectroscopy DCP¹².

Effect of heating rate: The heating rate is among important parameters in the thermogravimetric analysis¹⁻⁴ so we studied its influence to the thermal decomposition of present samples.

In the object to study the effect of this parameter we proceeded to the slow pyrolysis of the new oil and all samples of oil in use in dynamic regime and under the same operating conditions with different heating rates *i.e.*, 5 °C min⁻¹ until 25 °C min⁻¹ with a landing of 5 °C min⁻¹. These heating rates were kept constant throughout each dynamic experiment.

Fig. 3 represents the thermograms of the new oil associate to different heating rates.

TABLE-1
TEMPERATURES OF THERMAL DEGRADATION BEGINNING (Td) AND
SOLID RESIDUAL RATES BY PYROLYSIS OF ALL OIL SAMPLES

Parameters	Working hours of engine										
	0	100	200	300	400	500	600	700	800	900	1000
Td (°C)	240	228	220	217	215	213	210	207	205	202	194
Solid residue (%)	1.47	2.29	2.57	2.85	3.14	3.69	3.89	4.44	4.72	5.00	5.43

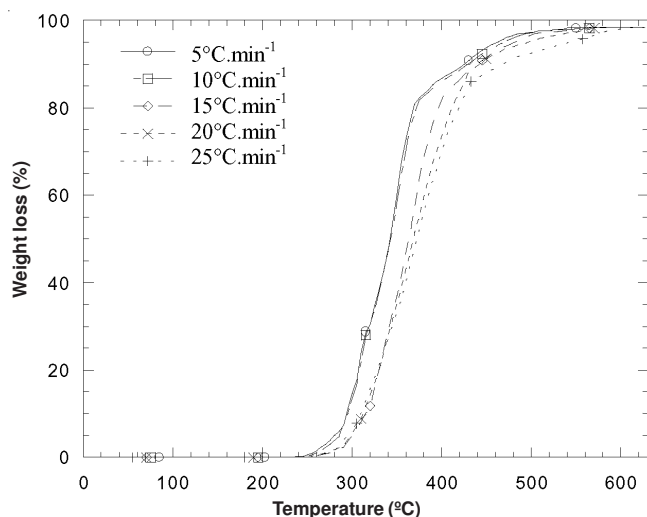


Fig. 3. TGA curves of new oil for different heating rates in inert atmosphere

We recover good that an increase of the heating rate leads the thermograms to move toward the height temperatures. For heating rates 5 and 10 °C min⁻¹ curves are practically superimposable. So the heating rate effect becomes insensible below 10 °C min⁻¹. However, above 15 °C/min the superposition of curves is just observed between 240 and 360 °C. But beyond of 360 °C curves are separated and the heating rate effect becomes perceptible. Therefore we can advance that the heating rate probably has not influence on the lightest VOF, but affects the cracking phenomenon of the main molecular chain. It is also noticed that the solid residual remains unaltered inspite of the variation of heating rate.

In order to well understand the phenomenon of oil decomposition we regrouped in the Fig. 4 the DTG curves of the new oil for all studied heating rates.

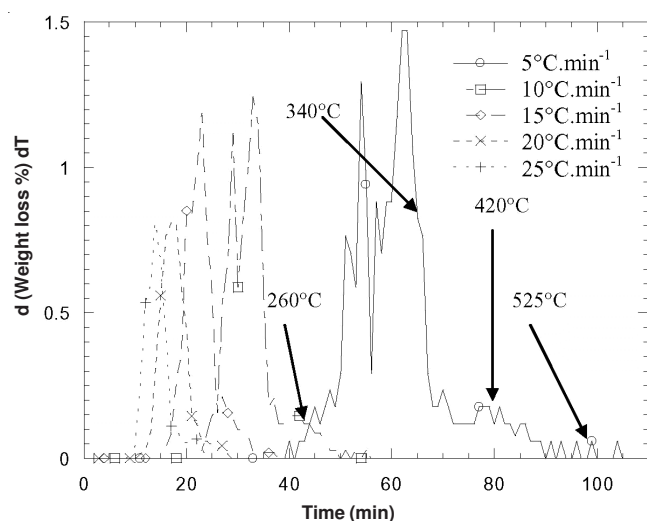


Fig. 4. DTG curves of new oil pyrolysis for different heating rates in inert atmosphere

It is noted that when the heating rate decreases thermograms present more thermal accidents. It is suggested that the thermal decomposition phenomenon becomes very lucid if we use a weak heating rate. Indeed, when the heating rate decreases the number of peaks observed increases, hence the

pyrolysis stages of new oil become separable. Besides for elevated heating rates phenomena become overlap. The pyrolysis reaction doesn't take time to free progressively the different families of VOF.

For heating rate of 5 °C min⁻¹ the analysis of thermogram shows that: (a) Between 260 and 340 °C the thermogram presents four different peaks. So the lightest VOF is formed by four different families. (b) Between 420 and 525 °C, it is noticed that the appearance of several micro-peaks presenting the polycondensation phenomenon. Indeed, the macromolecules resulted by the main chain cracking at the thermal decomposition ending would be assembled and would have undergone polycondensations to form the solid residual mass. This phenomenon is practically observed in the internal combustion engine.

In the hottest areas of diesel engine lubricating oil undergoes the polycondensation phenomenon. This phenomenon leads an increasing of the viscosity. Otherwise the highest peak of every DTG curves which corresponds to the maximal decomposition has a decreasing evolution as a function of the heating rate.

Oil in use loses progressively its lubricating power. Hence we are interested to study the influence of heating rate for oil samples after 500 and 1000 working hours of engine.

Figs. 5 and 6 represent, respectively the TGA and DTG tracings of oil after 500 working hours of engine in use. It is noted that the gotten thermograms present the same pace. The effect of this factor is appeared by a curves displacement toward the higher temperatures when the heating rate increases. Besides, the pyrolysis phenomenon can be illustrated well if we use a low heating rate. Indeed in present study for 5 °C min⁻¹ the DTG curve contains more peaks.

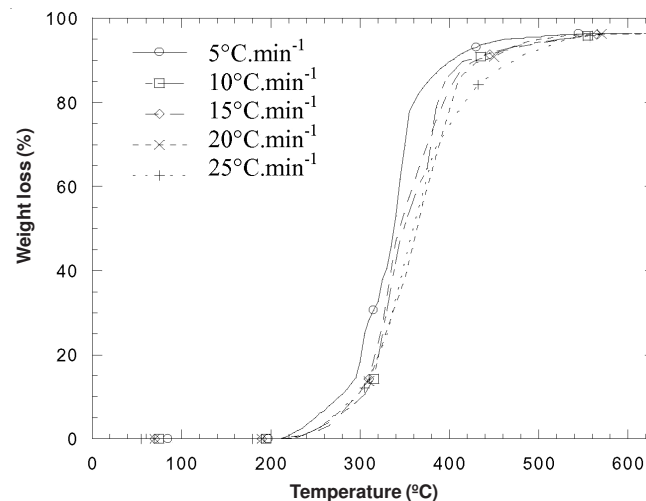


Fig. 5. TGA curves of oil in use 500 WHE for different heating rates in inert atmosphere

Between 250 and 325 °C, it is noted that for 5 °C min⁻¹ the DTG thermogram presents three different peaks. Hence the lightest VOF contain three families. The presence of micro-picks reflecting the phenomenon of polycondensation between 420 and 510 °C is observed.

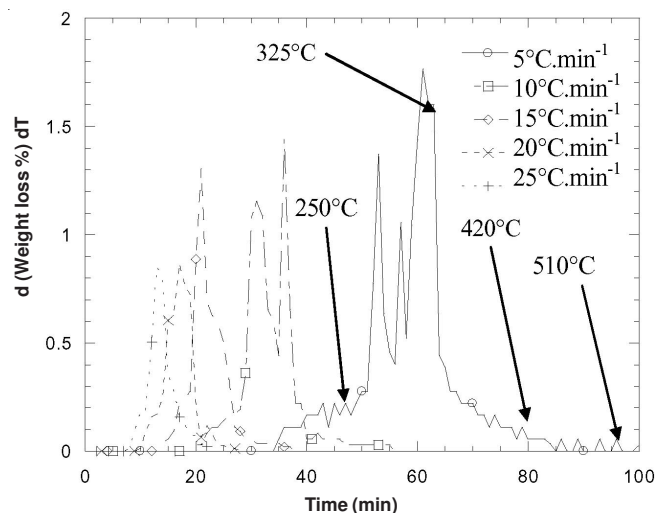


Fig. 6. DTG curves of oil in use 500 WHE for different heating rates in inert atmosphere

Besides, the highest peak (corresponding to the maximum of decomposition) for every DTG diagram presents a decreasing evolution according to the heating rate. In the same way as previously, we analyzed oil in use having done 1000 working hours of engine with the different heating rates studied. The results are indicated by Figs. 7 and 8.

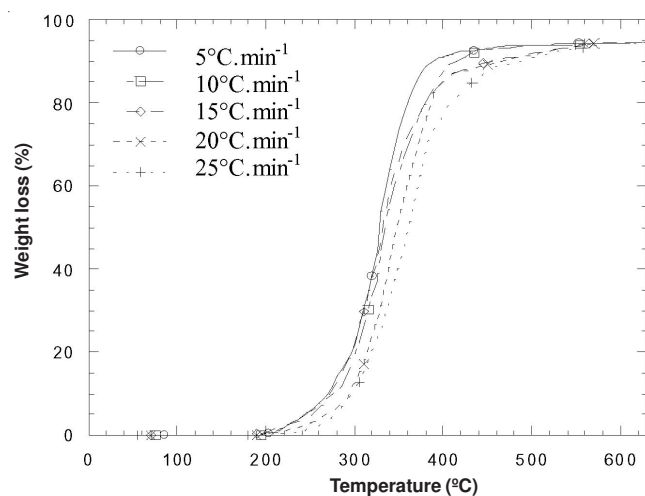


Fig. 7. TGA curves of oil in use 1000 WHE for different heating rates in inert atmosphere

The thermograms of the Fig. 7 indicate that the thermal decomposition of this sample is sensitive to heating rate variation. For the weakest heating rates the thermal degradation of oil in use 1000 working hours becomes clearer. It is clearly visible on the DTG diagram relating to 5 °C min^{-1} (Fig. 8). For this curve in addition to the peak associated to the maximum of the material degradation it is noted that apparition of two other peaks having low intensities marking the departure of lightest VOF so we can affirm that oil in use having done 1000 working hours of engine contains three families of VOF. At the end of the pyrolysis reaction we note the presence of macromolecules polycondensation which give the solid residual mass.

The analysis of DTG of pyrolysis of oils in use after 500 and 1000 working hours of engine permits to clear the

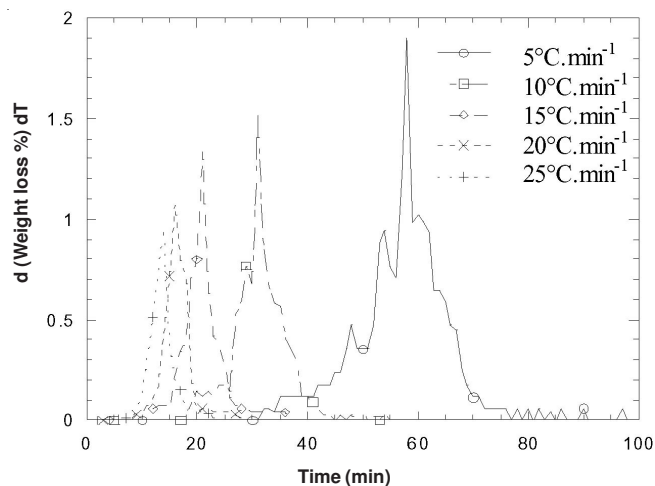


Fig. 8. DTG curves of oil in use 1000 WHE for different heating rates in inert atmosphere

following points: (a) The intensity of the peak indicating the maximum decomposition is progressively increasing when oil lubricates the engine. (b) The temperature of maximal decomposition is progressively decreasing when the working hours are increasing. (c) The number and the form of thermal accidents appearing before the maximal decomposition are note the same for 500 and 1000 working hours of engine.

We can then advance that the observed increase of the peak intensity is explained by the progressive loss of the lubricant power and the increase of metallic particles concentration in oil when the working hours of engine rises. Therefore more the number of working hours is increasing the temperature of maximal decomposition decreases and oil in use becomes thermally unstable. Besides, the lightest VOF become affected by the ageing.

It is also noticed that the intensity of the peak indicating the maximal decomposition of every DTG diagram is decreasing as function to the heating rate.

Conclusion

The study of the heating rate effect suggested that the thermogravimetric analysis with low heating rate shells well the phenomena accompanying the thermal decomposition of lubricant oil by pyrolysis. For 5 °C min^{-1} heating rate the comparison of the results of DTG of the new oil and oils in use having done respectively after 500 and 1000 working hours of engine shows an important increase of the highest peak according to the engine's working hours. This counterpart the highest peak's temperature is decreasing when the oil in use lubricates more the engine. It is presumed that the increase of working hours makes oil to free the VOF with higher velocity and at weaker temperature. Consequently more the number of working hours is increasing oil loses progressively its initial lubricant power. At the side of the higher the concentration of metallic particles in oil is, the faster the oil degradation becomes¹².

Otherwise, we noticed that the number of peaks relating to de VOF clearing is progressively decreasing according to the engine work hours. So, the lubricant oil loses progressively its initial structure during the diesel engine lubrication.

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