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HIGH-RESOLUTION TG FOR THE CHARACTERIZATION OF DIESEL FUEL ADDITIVES

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Abstract

High-resolution thermogravimetric analysis (Hi-Res^{TM} TG) in its variable heating rate mode was applied to commercially available diesel fuel additives under a nitrogen atmosphere. A TGA 2950 from TA Instruments was used to run the experiments. For the selected diesel fuel additives, the use of variable heating rate resulted in sharper transitions and clearer onset of degradation than in traditional constant heating rate experiments. Moreover, the time required for experiments giving reasonable resolution was remarkably reduced compared to constant heating rate experiments. The technique proved to be very useful in the study of multi-component systems, such as diesel fuel additives, since it provides more detailed information regarding mass changes in the sample as a result of heat treatment when total decomposition involves more than one stage i.e. mass changes stem from consecutive reactions.

Keywords: diesel fuel additives, high-resolution TG, thermogravimetry

Introduction

Additives have been used for many years to maintain or enhance various diesel fuel quality characteristics. Precombustion diesel fuel additives may be added to ensure that the fuel does not deteriorate on storage, that it is free from problems during distribution and that deposit formation and corrosion does not occur in the fuel system of an engine. They may also be required for marketing or legal reasons [1]. In addition, additives influencing the combustion processes may be present in diesel fuels. For instance, cetane number improvers are used to upgrade diesel fuel quality in term of ignition performance, diesel detergents are used to reduce nozzle coking whereas diesel smoke suppressants are effective in reducing smoke emissions [2, 3].

Additives may consist of a single chemical compound or involve up to a dozen components. The complexity is determined primarily by the combination of qualities desired by fuel manufacturers/suppliers. Multifunctional additives are quite in common to fit their individual needs. Most additives contain solvents or diluents to ensure easy handling and complete mixing in fuel as well as polymeric dispersants to improve fuel system cleanliness performance. Diesel fuel additives in Europe are for-

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mulated to be totally ashless and they must conform to the environmental regulations and not cause significant deterioration of air quality.

It is sometimes necessary or desirable to be able to analyse a diesel fuel to see what type and concentration of additive is present. To carry out such analyses is extremely difficult, particularly if one attempts to identify the nature and concentration of an unknown additive. Some oil companies may use precise formulations of definite additives and in the case the neat additives are available chemical analyses are easier to perform. Since they usually involve thermal separation methods, an understanding of the thermal behaviour of diesel fuel additives is essential.

Thermogravimetric analysis (TG) is increasingly used as a rapid, automated gravimetric technique to separate complex mixtures according to differences in volatility, pyrolysis or oxidation behaviour [4, 5]. In conventional TG the sample is made to follow a predetermined, usually linear, temperature program while mass loss is measured. Often, the decomposition steps cannot be separated due to parallel or consecutive reactions. To improve resolution new techniques have been developed in which variable heating rates are used [6]. These differ from conventional TG in that the heating rate is not predefined but continuously varied in response to the rate of change of sample mass (dynamic rate TG). The high-resolution TG technique of TA Instruments (Hi-Res^{TM} TG) uses in the dynamic rate approach a mathematical function to relate the rate of change of sample mass to the sample heating rate [7, 8]. As the rate of change of sample mass increases the heating rate is decreased, the result being a lowered heating rate through each decomposition step. Since this technique allows high heating rates to be used in regions where no mass changes occurr, it provides a good compromise between improved resolution and analysis time.

In this investigation, commercially available multifunctional diesel fuel additives from different suppliers have been analysed using Hi-Res^{TM} TG in the dynamic rate approach. The technique can assist the chemist in characterizing fuel additives with respect to its propensity to volatilize/decompose. This investigation is part of a larger study on the characterization of additives using instrumental methods with the aim of gaining knowledge of their function under end-use conditions.

Experimental

Materials

The following five commercial additives for diesel fuels were considered in this investigation:

Additive *A*: additive package for low-temperature operability (cold flow improver) containing wax anti-settling additives (WASA).

Additive *B*: multifunctional additive which acts as cetane number improver, diesel detergent and diesel smoke suppressant. Moreover, it contains antioxidants to prevent oxidative deterioration during storage as well as biocides to inhibit growth of bacteria or fungi in storage tank bottoms.

Additive *C*: multifunctional additive which, besides the operational features of *B,* is promoted as an excellent cold flow improver.

Additive *D*: multifunctional additive which contains a dispersant for engine cleanliness, an antifoam agent to reduce foaming tendency, a corrosion inhibitor for rust prevention, a demulsifier for good water separation and an antioxidant for fuel storage stability.

Additive *E*: lubricity additive designed for application in standard 0.05% sulphur EN 590 diesel fuel to protect from pump wear. Apart from its lubricity performance, it is marketed as a highly effective corrosion inhibitor and demulsifier.

Instrumentation and procedure

The measurements were performed using a Thermogravimetric Analyzer (TGA) 2950 from TA Instruments with Hi-Res^{TM} option. The TGA 2950 was used to measure the mass loss profile of the fuel additives in both the high-resolution (dynamic heating rate) mode and – for comparison purposes – in the conventional (constant heating rate) mode. Two experimental parameters need to be selected to perform a dynamic heating rate TG experiment – the initial (maximum) heating rate and the resolution ramp index. Another parameter – the sensitivity – is available for further fine tuning if required. The technique has been described in detail elsewhere [8]. For the experiments in the dynamic mode, the initial heating rate was 20°C min^{-1} whereas the settings used for the resolution ramp index and sensitivity were +4 and 2, respectively. The selected conditions were a reflection of the need to obtain well resolved mass loss steps as well as to avoid long analysis time. The heating rate in the conventional mode was 5°C min^{-1}.

All scans were carried out using samples of 80–100 mg from ambient temperature to 600°C under a nitrogen atmosphere at a purge rate of 80 mL min^{-1}. A ceramic crucible of 250 μL was used and flame-cleaned prior to each scan. Before starting the experiments the instrument was calibrated for temperature readings and buoyancy effects. Data analysis was performed using TA Instruments Thermal Solutions software.

Results and discussion

Figure 1 shows the TG curve for additive *A* resulting from conventional TG at 5°C min^{-1}. In addition to the mass loss, the heating rate and the temperature derivative of mass loss (DTG) are displayed as a function of temperature. The derivative profile indicates that the additive decomposes in two or perhaps three main steps between room temperature and 500°C, with a predominant decomposition occurring over the range 70 to 200°C due to solvent evaporation and with a further less pronounced decomposition beginning at 350°C mainly due to thermal degradation (pyrolysis) of neat additive compounds, to leave behind some carbonaceous material. As the first mass loss is not complete before the second mass loss begins, which in turn seems to run into a third mass loss, the decomposition steps are difficult to be quantified even

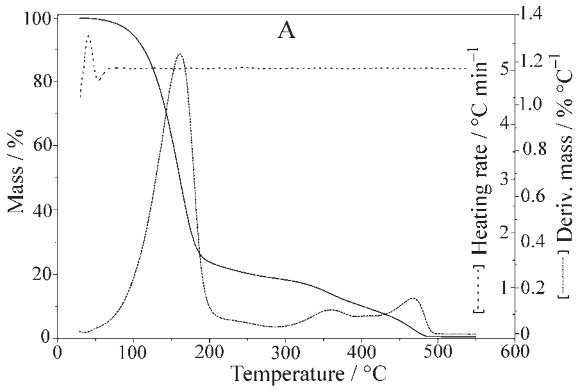

Fig. 1 Conventional TG for additive *A* using a heating rate of 5°C min^{-1} under a nitrogen atmosphere

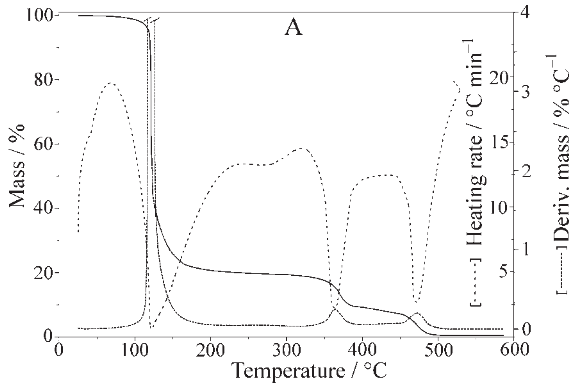

Fig. 2 High-resolution TG for additive *A* using an initial heating rate of 20°C min^{-1}, a resolution ramp index of +4 and a sensitivity of 2 under a nitrogen atmosphere

using the derivative curve. In the high-resolution mode, however, the DTG peaks are narrower and more intense than those obtained from conventional TG, because the technique permits continuous, smooth variation of the heating rate in response to the sample's measured rate of mass loss. Consequently, the decomposition steps occur at lower temperature and over smaller temperature ranges (Fig. 2). A first stage of mass loss, which occurs between 90°C and 130°C displaying a distinct DTG-peak with peak maximum at 110°C, is followed by a slightly gradual decline in the TG curve containing two further, rather small stages of mass loss. This is shown in the DTG curve by small, but well separated peaks with peak maxima at 370 and 470°C indicating the degradation of the polymeric compounds typical of flow improvers and wax modifiers [1]. The inflection points within the derivative curve were used to determine the percentage mass loss due to the decomposition steps. The percentage mass loss, the temperature range of decomposition and the residue content are given in Table 1.

Table 1 Compositional analysis of the additive samples by high-resolution TG in the dynamic heating rate mode under a nitrogen atmosphere (initial heating rate=20°C min^{-1}, resolution ramp index=+4, sensitivity=2)

Additive	Temperature range of decomposition/°C				Mass loss/%				Residue/% (at 600°C)
	step 1 (≤200°C)	step 2 (≤300°C)	step 3 (≤400°C)	step 4 (≤500°C)	step 1	step 2	step 3	step 4	
A	105–160	–	350–380	460–490	72.7	–	5.4	6.0	0.5
B	85–130	200–260	–	360–445	79.3	5.1	–	9.5	0.7
C	80–140	170–230	–	440–490	50.2	38.9	–	3.1	0.6
D	90–200	220–300	350–390	420–460	39.4	44.7	6.0	3.6	0.9
E	90–120	180–260	–	370–460	13.5	62.8	–	10.3	1.0

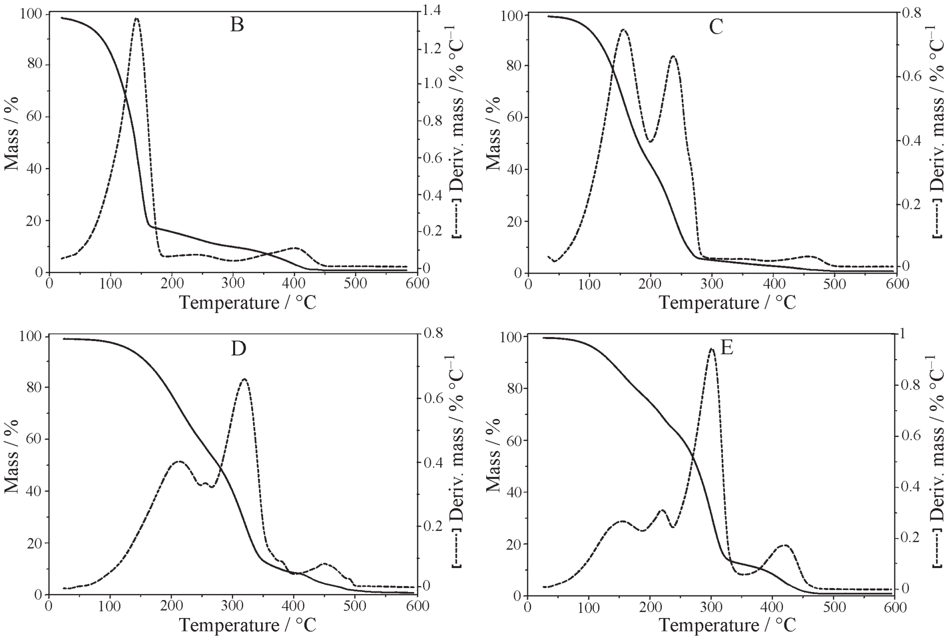

Fig. 3 Mass loss profiles and DTG curves for the additives *B–E* in the conventional mode (heating rate=5°C min^{-1}) under a nitrogen atmosphere

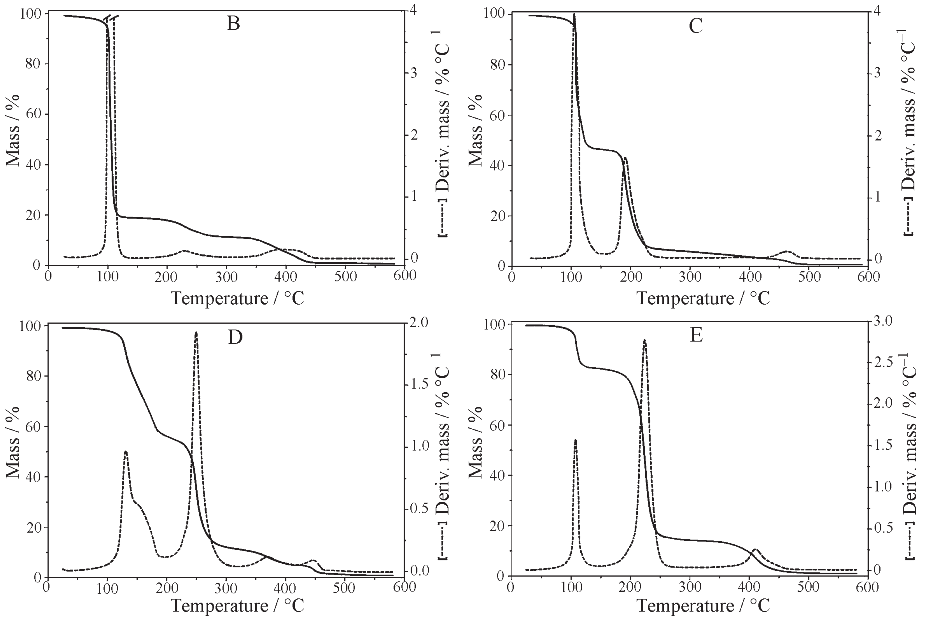

Fig. 4 Mass loss profiles and DTG curves for the additives *B–E* in the high-resolution mode using an initial heating rate of 20°C min^{-1}, a resolution ramp index of +4 and a sensitivity of 2 under a nitrogen atmosphere

The TG profiles together with the DTG profiles of additives *B–E* obtained in the conventional mode and in the high-resolution mode are displayed in Figs 3 and 4, respectively. Poorly resolved events can easily be seen in the DTG profiles of the conventional TG experiments, where the signal between two peaks does not return to baseline, or one of the events appears as a shoulder. Enhanced separation can be achieved by the dynamic heating rate experiments in even less measuring time than the 115 min needed for the complete scan at 5°C min^{-1}. In fact, for the five samples chosen, the time elapsed during the dynamic heating rate scans was about 90 min, when using the experimental parameters stated above.

The TG profile of additive *B* clearly demonstrates the difference in resolution between the two methods especially during the loss of low-boiling solvent up to 180°C. Only in the high-resolution mode does the TG profile show a well-defined mass loss step and a sharply resolved peak in the derivative curve which provides easy quantification of solvent loss. Apart from this main peak with a comparably high maximum rate of mass loss at 110°C, the DTG curve of additive *B* displays two well-separated humps with maxima at 230 and 400°C. The mass loss associated with these humps is so small and gradual that it cannot be quantified using conventional TG. The first hump can be partly attributed to octyl nitrate cetane improvers, which are marketed by major additive companies [1]. Their presence was confirmed by the use of infrared spectroscopy being the absorbance band at 1640 cm^{-1} a clear indication of the presence of alkyl nitrate compounds. The mass loss occurring within the rather broad temperature interval of 350–450°C is probably due to the simultaneous decomposition of various additive components, such as polymeric dispersants, antioxidants and diesel smoke suppressants.

The gradual decline of the conventional TG profiles of additives *C* and *E* between 100 and 300°C is resolved in the dynamic heating rate experiment into two well pronounced steps below and above 150°C. This indicates the presence of a co-solvent, which must be used in certain cases to achieve compatibility of neat multifunctional additives [3]. Additive *E* differs from additive *C* mainly by the fact that the first peak is smaller and the second larger and shifted towards higher temperature by about 30°C.

As far as additive *D* is concerned, the improved resolution obtained in the high-resolution mode makes it potentially easier to quantify the various mass losses, even if in this case the thermal events are not completely separated. The DTG profile of additive *D* exhibits in the high-resolution mode a first peak with a maximum at 130 and a high temperature shoulder, a rather sharp second peak with a maximum at 250, a third small peak between 350 and 390, and a separate fourth peak over 420°C. All that reflects the complexity of this additive package.

Table 1 summarizes the thermogravimetric results for the main stages of mass loss. The additive samples differ markedly in their contents of solvent, neat additive compounds and residue. Additive *E* has the highest residue content whereas additive *C* has the highest content of total solvent (step 1+step 2) and the lowest content of neat additive compounds (step 4).

Conclusions

The results obtained in this research for the selected additives provide convincing evidence that high-resolution TG is a suitable technique for characterizing additives with respect to their propensity to volatilize/decompose. In the dynamic heating rate mode, high-resolution TG experiments take generally less time to complete than comparable constant heating rate experiments, while providing improved resolution. Resolution of successive TG mass losses aids in characterizing complex thermal decomposition processes. In addition, the technique operates under conditions close to equilibrium because of the comparatively low heating rate used where mass changes are occurring. One can obtain accurate measurements of mass change and reaction temperature even of consecutive thermal events, which makes this technique particularly useful for material compositional analysis and for comparison of competitive products.

Despite the fact that resolution in conventional, linearly heated, TG can be significantly enhanced by mixing isothermal holds periods into the temperature program based on previous experience with the material, the high-resolution approach is self-adapting and hence more flexible in its application. However, taking into account the broad number of compounds that are present in additives, it is only by the combination of the results from thermogravimetry with other separation techniques and detection techniques that complete qualitative and quantitative information can be obtained.

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