Journal of Thermal Analysis and Calorimetry, Vol. 56 (1999) 1389-1396

THERMOGRAVIMETRIC FOURIER TRANSFORM INFRARED SPECTROSCOPY OF HYDROCARBON FUEL RESIDUES

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Abstract

Although thermogravimetric analysis (TG) has become an indispensable tool for the analysis and characterization of materials, its scope is limited as no information is obtained about the qualitative aspects of the evolved gases during the thermal decomposition. For processes involving mass loss, a powerful technique to provide this missing information is Fourier transform infrared spectroscopy (FT-IR) in combination with TG. It supplies a comprehensive understanding of thermal events in a reliable and meaningful way as data are obtained from a single sample under the same conditions.

The coupling TG/FT-IR is used in fuel analysis for the identification of residual volatiles, to determine their sequence of release and to resolve thermogravimetric curves. In this work, the usefulness of TG/FT-IR for characterizing middle distillate fuel residues is illustrated with some typical examples of recent application. A Bio-Rad FTS 25 FT-IR spectrometer coupled with a TA Instruments TGA 2950 thermogravimetric analyzer was used for data aquisition.

The results obtained demonstrate the utility of this combined technique in determining the decomposition pathway of tarry materials at various stages of pyrolysis, thereby allowing new insights into the complex thermal behaviour of hydrocarbon residual systems.

Keywords: FT-IR, fuel, oil, pyrolysis, residue, TG

Introduction

Thermogravimetric analysis (TG) provides information regarding mass changes in the sample resulting from heat treatment under controlled environment. However, it gives no indication of the type of gases evolved during the thermal decomposition. In many cases, such information can be very valuable, especially when several gases are simultaneously evolved during one mass loss [1]. Relatively simple gases, such as water vapour, methane, formaldehyde, oxides of carbon etc., are easily identified by FT-IR analysis of the evolved gas flow, even if they are evolved together, because of their characteristic absorption frequencies and band contours [2, 3]. In more complex products, such as fossile fuels, the observed group frequencies are often enough to define the chemical class, even if total identification is not achieved [4, 5].

1418-2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Deposit formation in fuels is mainly the result of fuel degradation and principally depends on the hydrocarbon composition, source of crude oil, type and severity of the refining process, and on the environment to which the fuel is exposed. Degradation is observed to occur under long-term low-temperature storage conditions (storage instability) [6, 7] as well as short-term high-temperature stress (thermal-oxidative instability) [7]. The main practical consequence of both storage and thermal-oxidative instability are the formation of harmful deposits in fuel tanks, distribution systems and injector nozzles, ultimately leading to malfunctions of the fuel system components and/or burner operating difficulties [8].

The primary objective of this investigation was to analyze and compare both the gas evolved as well as changes in the mass of fuel residues during thermal decomposition under nitrogen and oxygen atmosphere. Specifically, the pyrolysis and subsequent combustion of residues coming from commercial heating oils are illustrated.

Experimental

Materials

Five residuals from commercial heating oils for atomizing type burners were considered in this investigation (Table 1). Sample *Ih*, *Ho* and *At* were collected as settled material from the bottom of three different vessels and should be characteristic of degradation products in storage tanks. Sample *Ko* was removed from a clogged filter of an intake system connecting the heating oil storage tank to the burner. It should contain degradation products of the fuel due to both storage and thermal instability as well as dirt, rust and other corrosion products that are frequently found in distribution systems. Sample *Oe* was collected from injection nozzles of a fouled burner system and its formation can be attributed to degradation products of the fuel due to thermal instability.

Prior to analysis, all samples were washed with pentane to remove remaining trace of fuel and then dried at 50°C until constant mass was achieved. Elemental composition of the deposits was determined using a Carlo Erba CHNS-O EA 1108 Elemental Analyzer. The results are given in Table 1.

Table 1 Ultimate analysis data of the selected heating oil residues

Parameter	*Ih*	*Ho*	*At*	*Ko*	*Oe*
Appearance*/%	Black, greasy paste	Brown to dark tar	Dark coloured resin	Black varnish	Black, hard brittle solid
Carbon	88.8	62.7	58.5	42.4	72.4
Hydrogen	7.9	6.6	6.5	3.9	0.49
Nitrogen	0.2	0.8	0.4	1.3	0.7
Sulfur	0.1	0.2	0.3	0.9	3.2
Oxygen	2.0	16.0	12.1	14.7	8.0

*after washing with pentane and drying at 50°C

Instrumentation and procedure

The TG/FT-IR system consisted of a TA Instruments TGA 2950 system interfaced with a Bio-Rad FTS 25 FT-IR spectrometer. The TG unit was equipped with an evolved gas analysis furnace, whose outlet was connected to the FT-IR by an interface consisting of a transfer line and a gas analysis cell both heated up (210°C) to prevent condensation. The gas cell, which has double windows at both ends (ZnSe inside, KBr outside), was equipped with a thermoelectrically cooled DTSG (deuterated triglycine sulfate) detector.

A multi-step heating program with isothermal holds was employed, during which the furnace was purged with 80 mL min^{-1} N_2 for drying/pyrolysis and O_2 for incineration. Automatic purge gas change was provided by the TA Gas Switching Accessory. The inert working conditions of the TG equipment with nitrogen were checked by measuring the rate of mass loss of a standard carbon black at 900°C. A maximum figure of 0.3 μg min^{-1} was considered acceptable. The temperature calibration was performed using the melting point of pure aluminium metal (660°C). Typical size of samples used in the experiments was about 100 mg.

The material was placed in a 500 μL ceramic pan and, after closing the furnace, held at 30°C in flowing nitrogen for 10 min to purge the system of all air. The temperature was ramped at 20°C min^{-1} to 110°C and held isothermally for 20 min, with the mass loss reported as moisture. The temperature was then ramped to 900°C at 20°C min^{-1} and maintained for 20 min. The mass loss at the end of this period was reported as volatile matter. After this isothermal phase the furnace atmosphere was changed to flowing oxygen and the temperature held constant for 15 min to determine the fixed carbon (coke), which was burned off, leaving the ash as residue.

Thermogravimetric data analysis was performed using TA Instruments Thermal Solutions software. The spectra of gaseous species evolving from the TG system were recorded and analyzed using Bio-Rad Win-IR software. All spectra were collected at a 4 cm^{-1} resolution over the range of 4000–600 cm^{-1}, co-adding 28 scans into a single trace file during a time intervall of 60 s. The single trace files collected throughout the total run time of the experiment of about 100 min were sequentially grouped into a multifile to obtain the evolved gas profile as a function of time.

Results and discussion

The TG profiles of the five samples under nitrogen atmosphere and during incineration are shown in Fig. 1. Table 2 summarizes the TG results for the decomposition stages as stated above. As expected, the deposits differ in their moisture, volatile matter, coke and inorganic residue content (ash). The high ash content of the deposits *Ko* and *Oe* can be ascribed to metal debris from the fuel system and removal of underlying metal when these samples were scraped from the fuel system components. Due to its low H/C ratio, sample *Oe* has by far the highest content of fixed carbon and the lowest content of volatiles. Conversely, sample *Ih* with its high H/C ratio (based on 100% organic material) has the lowest content of fixed carbon and the highest amount of volatile matter.

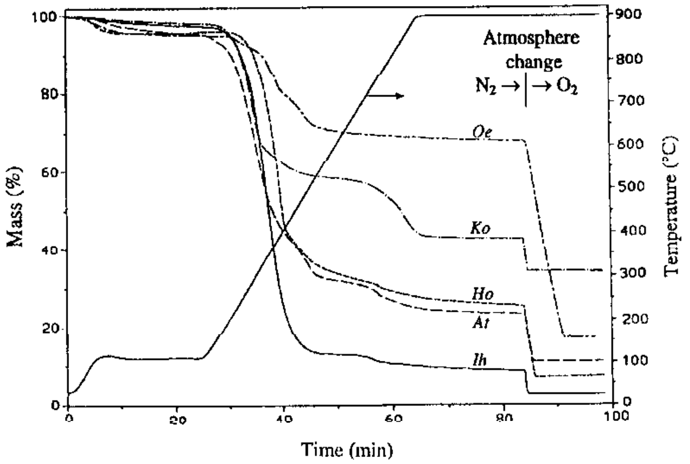

Fig. 1 Thermogravimetric profiles for the selected samples during thermal decomposition in nitrogen and incineration

Table 2 TG analysis data of the selected heating oil residues

Parameter /%	*Ih*	*Ho*	At	*Ko*	*Oe*
Moisture	2.6	4.1	4.7	1.9	4.6
Vol. matter	88.6	70.2	71.7	55.3	26.1
Fixed carbon	6.0	18.2	12.4	8.6	51.3
Ash	2.8	7.5	11.2	34.2	18.0

The differential TG profiles (d*W*/d*t* *vs.* time plots) during pyrolysis are displayed in Fig. 2. Contrary to the other samples, sample *Oe* displays no marked mass loss in nitrogen above 600°C (run time=50 min). It reveals in the derivative curve three mass loss events with peak maxima around 250, 380 and 480°C. Sample *Ko* exhibits a first distinct peak with a maximum at 300°C and a high temperature shoulder at 400°C as well as a rather broad peak with a low temperature shoulder at 780°C and a peak maximum at 850°C. The derivative curve of sample *At* is similar to that of sample *Oe* with three unresolved peaks below 600°C (150, 310, 500°C). In common to the other three samples, it displays, however, a separate peak over 700°C (760°C). The derivative curve of sample *Ih* shows a well resolved peak with a comparably high maximum rate of mass loss at 350°C and a hump at 730°C. Sample *Ho* differs from sample *Ih* mainly by the fact that both peak maxima are shifted towards higher temperature by about 30°C and it exhibits a sharper first peak with an inflection near 450°C.

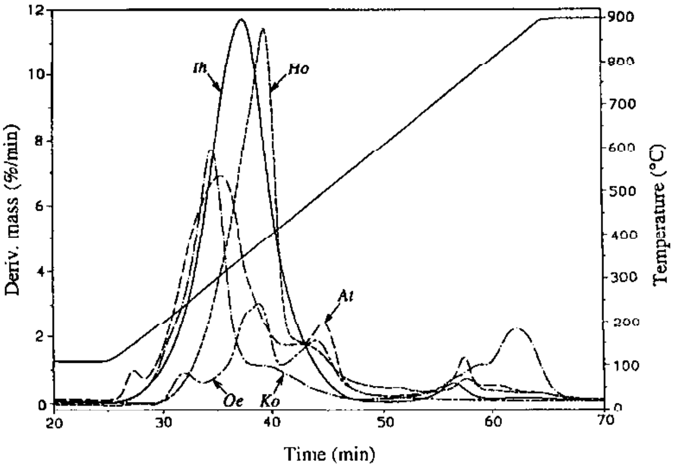

Fig. 2 Derivative TG curves for the selected samples during pyrolysis

Figure 3 shows three dimensional FT-IR spectra for the gases evolved during the TG scan from the five samples. The time scale of the perspective axis is correlated with the temperature by the heating rate used. Since there is some time delay for the gas between being released in the TG furnace and measured in the FT-IR cell, all FT-IR peaks appear at a slightly higher temperature than the maximum rates of mass loss displayed in the differential TG. In the course of the dehydratation step up to 110°C (run time≈25 min) the characteristic water bands (3950–3550, 1700–1300 cm^{-1}) can clearly be seen in samples *Ho*, *At*, and *Oe*, which is indicative for absorbed water or van der Waals water.

During pyrolysis, sample *Ih* shows strong C–H stretching peaks (aliphatic single bonds: 2950 and 2850 cm^{-1}) and the C–H bending peak (1450 cm^{-1}) indicating presence of short chain saturated aliphatic hydrocarbons. The 1350 cm^{-1} band arises presumably from the symmetric bending vibration of CH_3-C groups. In addition, the spectrum of evolved gases includes two unresolved peaks at 3100 and 3050 cm^{-1}, which may arise from aliphatic and/or aromatic –C=C–H streching, and a further weak band at 1650–1600 cm^{-1}, whose structural assignment is difficult. One may suppose that it comes either from aromatic or aliphatic –C=C– stretching. These findings indicate that pyrolysis products of sample *Ih* include saturated and unsaturated hydrocarbons as well as aromatic rings. Another gaseous component evolved is carbon dioxide (2400–2200 cm^{-1}), while water bands are missing completely. All this together with the results of the ultimate analysis suggests that residue *Ih* consists principally of (residual) oil sludge as a result of the fuel incompatibility with other fuels, with which it was blended, rather than of degradation products caused by storage instability.

The FT-IR spectrum of sample *Ho* shows C=O streching bands between 1800–1600 cm^{-1} and C–O stretching bands at 1300–1000 cm^{-1}. Ester, aldehydic, ketonic or carboxylic acid groups may therefore be present in this residue. The broad bands

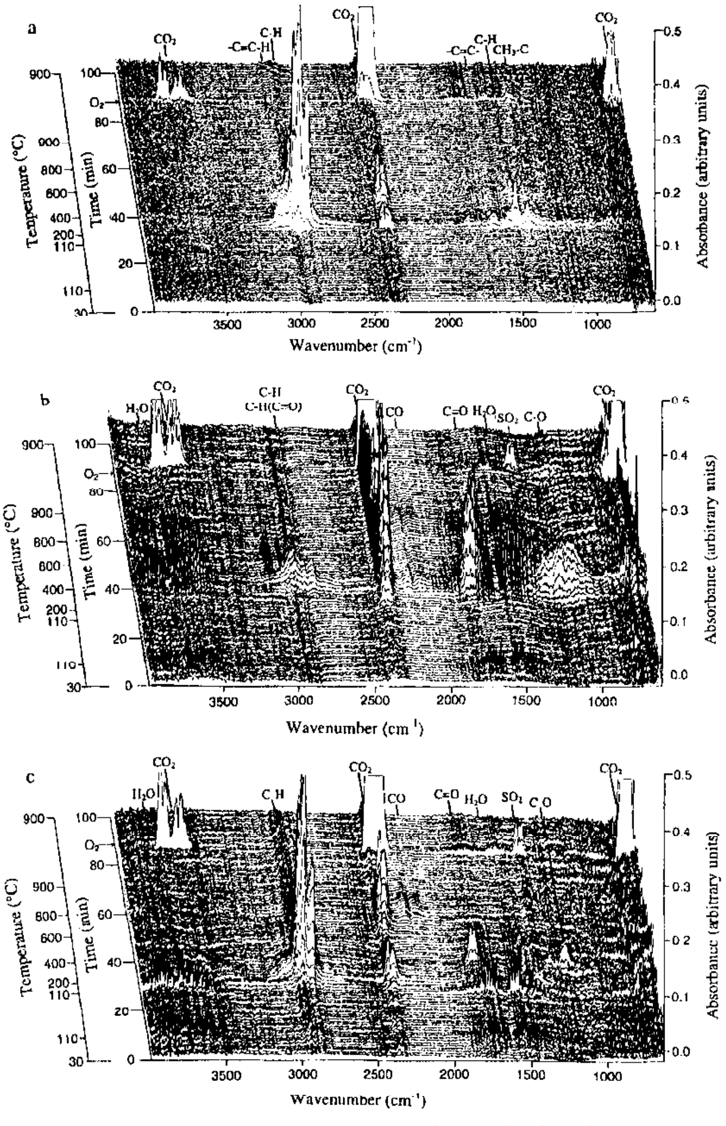

Fig. 3 Three-dimensional FT-IR absorption spectra of the evolved products: (a) sample *Ih*; (b) sample *Ho*; (c) sample *At*

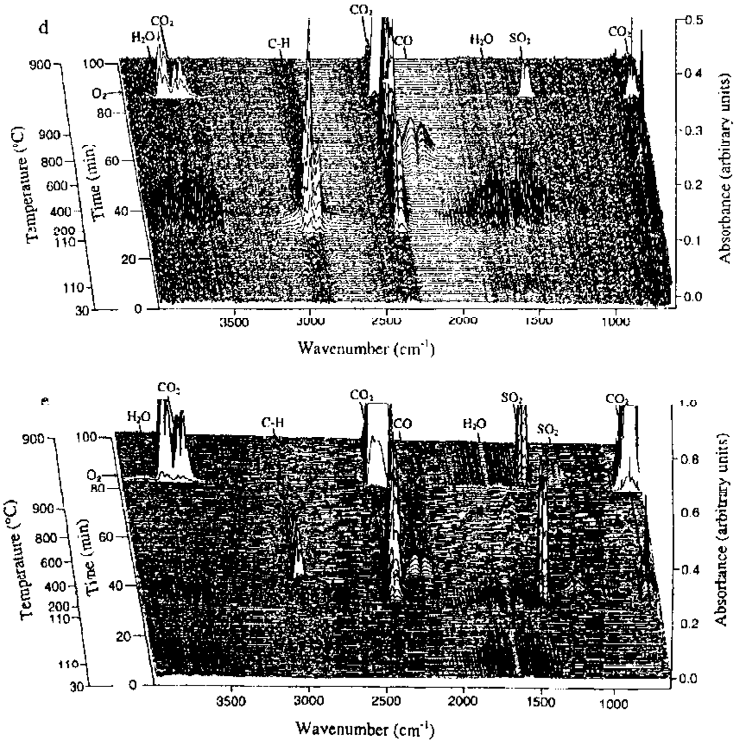

Fig. 3 Three-dimensional FT-IR absorption spectra of the evolved products: (d) sample *Ko*; (e) sample *Oe*

between 3000–2650 cm^{-1} are also indicative for carbonyl groups. The appearance of these bands can be attributed to the oxidation products of hydrocarbon components of the fuel. Other gaseous component evolved are easily identified as carbon dioxide (2400–2200 and 750–650 cm^{-1}) carbon monoxide (2200–2050 cm^{-1}), and water vapour (3700–3550, 1550–1350 cm^{-1}). As water begins being evolved at the relatively high temperature of 450°C, it may be deduced that this sample contains chemisorbed water.

The FT-IR spectrum of the pyrolysis of *At* is somewhat similar to that of sample *Ho*, but less oxygen containing species are produced during pyrolysis. Moreover, contrary to sample *Ho*, the much stronger C–H stretching vibration (2800–3000 cm^{-1}) indicates that an appreciable amount of hydrocarbons is released.

The FT-IR spectrum of gases evolved during the pyrolysis step of sample *Ko* is fairly simple. The characteristic peak locations indicate the presence of hydrocarbons, CO, CO_2 and water vapour. Thermal decomposition begins around 200° and shows a first maximum mass loss around 400°C due to the simultaneous release of hydrocarbons, lattice water, and CO_2. A second maximum mass loss is displayed at 800°C caused by the simultaneous evolution of CO and CO_2. The CO_2 absorption band at 2400–2200 cm^{-1} changed in intensity with increasing temperature. The two peak maxima observed suggest that the release of CO_2 occurs as a result of two different decomposition reactions.

The FT-IR spectral changes that occur in sample *Oe* during pyrolysis reflect the multi-stage decompositon pathway of this residue. In the initial stage of pyrolysis (300°C) the release of water vapour is predominant. At 400°C it follows SO_2 (1370 and 1100 cm^{-1}) accompanied by an initial loss of CO_2 and on further heating (500°C) the evolution of more CO_2 along with CO and some hydrocarbons are observed. The SO_2 peaks reflect the higher sulfur content of *Oe*. The spectrum obtained for this sample is typical for residues formed under high-temperature stress in an oxygen rich enviroment since such residues generally contain a considerable amount of oxidized fuel compounds and in particular hydrocarbons oligomers that decompose at relatively high temperature.

During incineration the largest portion of the mass loss is dominated by release of CO_2 (3700–3500, 2400–2200 and 750–650 cm^{-1}) from the combustion of fixed carbon. SO_2 bands can be observed in all samples except for sample *Ih*. Water bands are clearly visible in sample *Oe*, weak hydrocarbon bands in sample *At*, as the result of the release of entrapped gas after burning of fixed carbon.

Conclusions

TG/FT-IR can extend the compositional capabilities of TG since it produces excellent data on multiple components evolving from complex systems, such as fuel residues. Although additional experiments are needed to develop optimum conditions and parameters, the capability of simultaneous characterization of thermal behaviour and identification of the evolved compounds make TG/FT-IR valuable for extensive investigation of the decomposition pathway of fuel residues.

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