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THERMOGRAVIMETRIC CHARACTERIZATION OF SOME IRAQI BITUMENS

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ABSTRACT

The thermogravimetric analysis of various Iraqi bitumens was conducted by heating them in a stream of nitrogen or oxygen gas from room temperature to 800°C at a rate of 20°C min^{-1} while recording the partial weight loss at 100°C intervals in addition to the total weight loss. Isothermal measurements in nitrogen gas were also performed by heating the bitumens from room temperature to 165°C and holding isothermally at this level for 250 min. The resulting thermogravimetric curves provided well-defined data for the characterization and identification of the bitumens studied.

INTRODUCTION

Petroleum products, heavy crude oils and other bituminous accumulations are usually characterized by a number of physical as well as chemical methods [1]. The conventional viscosity and density as well as the various standard techniques are no longer sufficient for the complete characterization of these complex organic compounds.

Thermoanalytical techniques [2–9], such as differential scanning calorimetry (DSC), thermogravimetry (TG) and differential thermogravimetry (DTG) have been successfully applied in recent years for studying the thermal stability and weight loss characteristics of many petroleum-derived products.

Masek [10] characterized 15 bituminous materials from Czechoslovakian crudes by recording not only the total weight loss from 20 to 1000°C at a heating rate of 5°C min^{-1}, but also the partial weight loss at 25°C intervals, so as to locate the beginning and maximum of weight loss. He also used a thermobalance for determining the composition and the course of degasification of heavy coal tar and petroleum fractions by heating them in a stream of argon or air from 20 to 1000°C at 18 or 5°C min^{-1}, while recording the weight loss. The resulting thermogravimetric analysis curves provided a

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well-defined characterization of the samples with respect to overall loss of weight and location of the peak loss.

Bitumens derived from Iraqi Kirkuk crude were also studied [11] by the combined DTA–GC techniques. The TG results performed in an inert atmosphere were characterized by continuously increasing weight loss between 200 and 450°C with little further weight loss between 450 and 700°C and the final formation of 5–15% coke as residue.

Although the study of the weight loss characteristics (TG) will show that no two bitumens are alike, it is possible, however, to identify various bitumen types on the basis of the general shape of the thermogravimetric curves.

The present investigation involves the application of programmed thermogravimetry for the characterization of some Iraqi bitumens and correlation of the results obtained with some of their physicochemical characteristics.

EXPERIMENTAL

Samples

Four bitumens, two (K and Y) derived from crude oils, the third (H) occurring naturally and the fourth a blown asphalt derived from the K bitumen were all obtained from local refineries. The relevant data on these bitumens are presented in Table 1.

Apparatus

TG and DTG determinations were performed simultaneously on a Heraeus TA 500 thermal analyser. Metal analyses were carried out with a Pye-Unicam SP 9-800 atomic absorption spectrophotometer.

TABLE 1

Specifications of the bitumens studied

Specifications [a]	K	Y	H	Blown K (BK)
Penetration at 25°C	50	60	40	20–30
Flash point (°C minimum)	230	276	190	224
Softening point (°C)	55	56	41	80–90
Ductility in (cm) at 25°C (minimum)	100	100	—	39
Specific gravity at 15.6°C	1.0595	1.0599	1.0656	—
Solubility in CCl_4 (wt%, minimum)	99.5	99.5	99.0	99.5
Ni content (ppm)	66.6	55.1	52.9	46.8
V content (ppm)	230.7	243.9	321.1	176.7
Total S content (wt%)	5.0	8.0	7.5	4.0

[a] Measured according to ASTM standard methods.

Programme

Two heating programmes were selected for this investigation. The first involved heating the bitumen from room temperature to 165°C in an inert atmosphere of nitrogen gas then holding isothermally for 250 min. The second programme involved heating the bitumen non-isothermally from room temperature to 800°C in an atmosphere of nitrogen or oxygen gas.

In both programmes, samples weighing 5–10 mg were placed in a platinum crucible and heated at a rate of 20°C min^{-1} in the chosen gas atmosphere flowing at a rate of 25 cm^3 min^{-1}.

All results are the average of two determinations.

RESULTS AND DISCUSSION

Isothermal measurements

The measurements of minor losses in weight of the bitumens studied at low temperature are made possible by the high resolution of the thermobalance. The change in weight of the bitumens after a linear heating process in nitrogen gas from room temperature was followed isothermally, i.e., at a

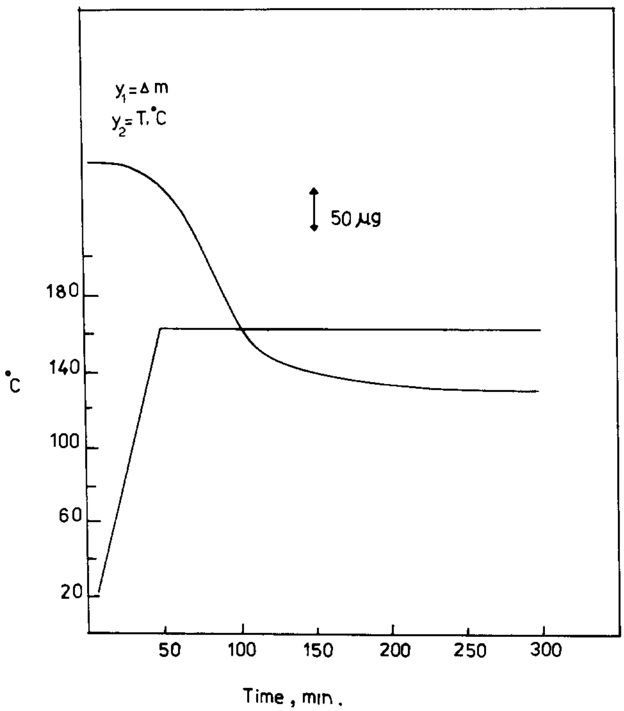

Fig. 1. Representative isothermal TG curve of the studied bitumens.

TABLE 2

Percentage weight lost on heating the bitumens using ASTM and thermogravimetric methods

Type of bitumen	% wt. lost, ASTM	% wt. lost, TG
K	1.0	1.1
Y	1.0	1.2
H	2.0	2.0
BK	9.6	9.8

constant temperature of 165°C for 250 min. This thermogravimetric curve usually gives information on the stability, preconditioning and thermal history of the sample. A representative isothermal curve related to the studied bitumens is shown in Fig. 1.

The percentage weight losses determined from these curves for the four bitumens studied are given in Table 2. The relative percentage weight losses on heating the same samples at 163°C for 5 h and as determined according to the standard ASTM method D-6 are also given in the same table. A good correlation was exhibited between the values of the results obtained from the two different techniques.

From Table 2 it is obvious that the blown asphalt possessed a somewhat higher percentage of volatile matter compared to the other bitumens studied. This may be attributed to the presence of large amounts of water in the form of an emulsion with the bitumen. This water is a by-product derived from the process of asphalt blowing. Meanwhile, the percentage of volatiles for the remaining bitumens ranged between 1 and 2% and are most probably a combination of moisture and hydrocarbon-type compounds.

Non-isothermal measurements

The main features of the non-isothermal thermogravimetric (TG) and differential thermogravimetric (DTG) curves of the bitumens studied performed in an atmosphere of nitrogen or oxygen gas between room temperature and 800°C are displayed in Figs. 2–5 and represent K, Y, H and blown K asphalt, respectively.

It is clear from these figures that under the inert atmosphere of nitrogen gas, the bitumens studied underwent volatilization which proceeded with a well-defined single, broad transition indicating a slow weight loss below 400°C and very rapid weight loss between 400 and 500°C. However, in the oxygen atmosphere, the thermogravimetric curves were of a rather complex nature indicating the presence of multiplet transitions occurring over a wide temperature range and are related to exothermal oxidation reactions which increased in intensity with increasing temperature. A rapid weight loss was again recorded in the 400–500°C region. It is also interesting to note from the TG curves of blown K (Fig. 5) the presence of an additional transition

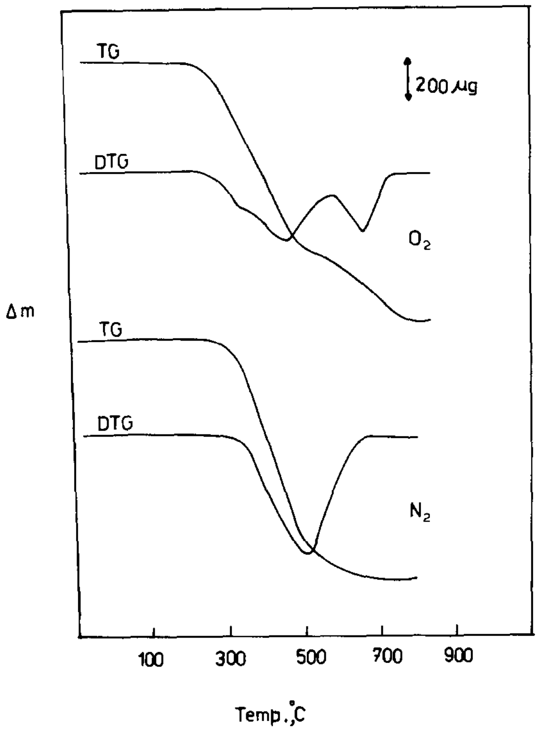

Fig. 2. TG and DTG curves of K bitumen in oxygen and nitrogen.

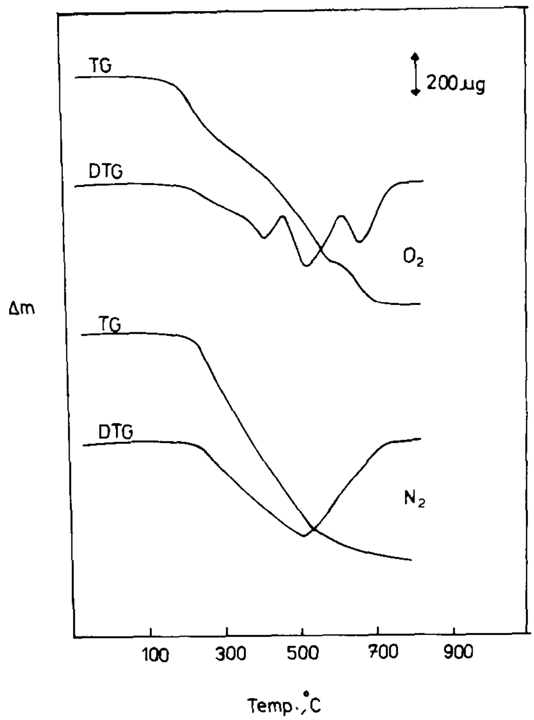

Fig. 3. TG and DTG curves of Y bitumen in oxygen and nitrogen.

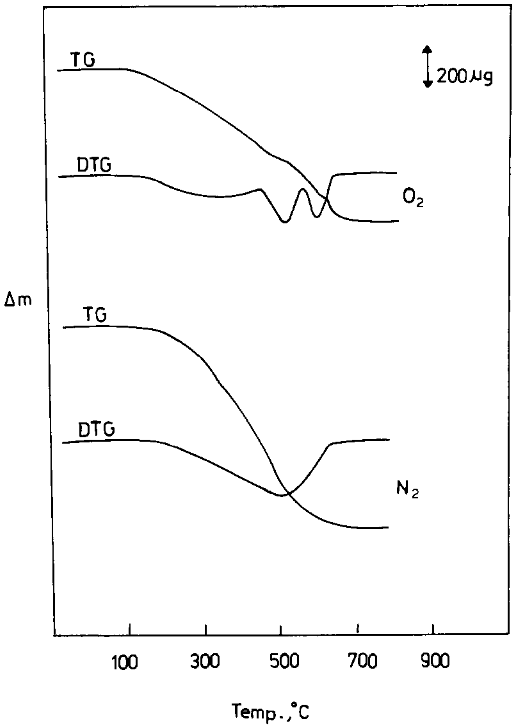

Fig. 4. TG and DTG curves of H bitumen in oxygen and nitrogen.

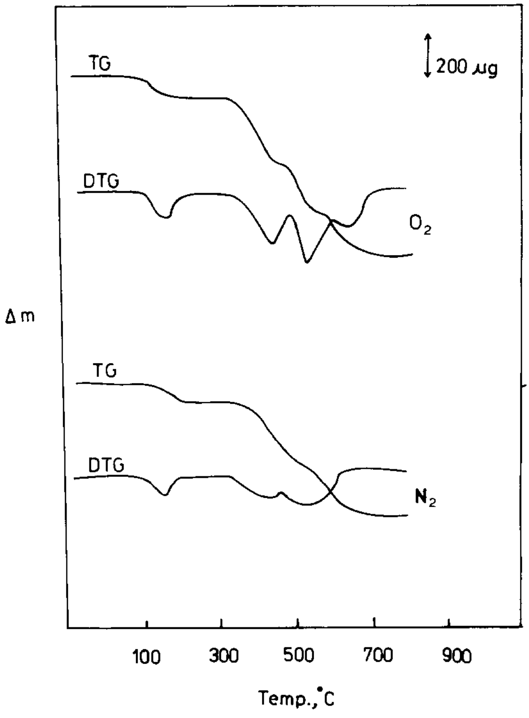

Fig. 5. TG and DTG curves of BK bitumen in oxygen and nitrogen.

TABLE 3

Thermogravimetric data[a] on the bitumens studied

Temp. range (°C)	% wt. lost in nitrogen				% wt. lost in oxygen			
	K	Y	H	BK	K	Y	H	BK
0–100	0	0	0	0	0	0	0	0
100–200	0	0	4.05	10.5	0	0	2.7	10.8
200–300	1.43	7.14	13.5	0	1.64	9.5	15.8	0.35
300–400	11.4	18.6	16.2	23.7	18.0	19.0	15.8	21.3
400–500	65.7	41.4	41.9	36.8	41.0	33.3	28.9	37.8
500–600	12.86	10.0	8.1	20.7	23.1	19.0	26.3	16.2
600–700	5.6	5.7	5.2	7.9	16.23	19.0	10.5	13.5
700–800	0.13	3.16	0.2	0.1	0	0.2	0	0.05
Residue, *R*	2.88	14.0	10.85	0.3	0	0	0	0

[a] From TG curves.

TABLE 4

Temperatures (°C) of transition of the bitumens studied obtained from DTG curves

Type of bitumen	T_i [a]	T_{max} [b] (nitrogen)	T_f [c]	T_i	T_{max} (oxygen)	T_f
K	300	510	635	250	—	700
Y	250	500	725	225	—	725
H	195	500	670	175	—	650
BK [d]	325	—	625	325	—	700

[a] Initial temperature of transition.
[b] Maximum temperature of transition.
[c] Final temperature of transition.
[d] The temperatures of transition due to volatilization of water are excluded.

between 110 and 170°C in O_2 and N_2 gas attributed to the loss of emulsified water present as a by-product from the process of blowing the K bitumen. The percentage weight loss involved in this transition is ~ 10.5% and is almost similar to that obtained from the corresponding isothermal measurement (9.8%). In addition, the exothermal oxidation reactions of the blown K started at a comparatively higher temperature (325°C) indicating the higher thermal stability of this product. Meanwhile, the major weight loss transition for the same bitumen recorded in N_2 gas showed discontinuity at 460°C.

The data extracted from the TG and DTG curves in nitrogen and oxygen atmospheres are displayed in Tables 3 and 4, indicating the percentage weight lost at 100°C intervals and the temperatures of transition of the major weight loss step, respectively.

The thermal data presented confirmed the fact that the maximum weight lost was recorded in the 400–500°C temperature region, as shown in Table 3.

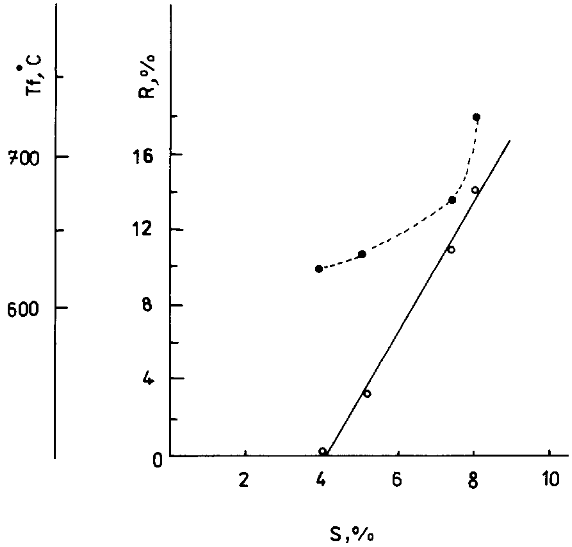

Fig. 6. Correlation between total sulfur content of the studied bitumens and the: (●) final temperature of transition (T_f) in nitrogen gas (○) residue (R) in nitrogen gas.

It is also worth noting that no residual matter remained at the end of the temperature programme when the thermogravimetric measurements on the bitumens were performed in oxygen, which is attributed to destructive oxidation with the final formation of water and carbon dioxide. However, a significant correlation was observed between the percentage of residue remaining when the measurements on the bitumens were performed in the inert atmosphere of nitrogen gas and their corresponding total sulfur content, i.e., BK asphalt with the lowest percentage residual content ($R = 0.3$) possessed the lowest sulfur content of 4%, whilst Y bitumen with the highest residual content of 14% had the highest percentage total sulfur content of 8%. This correlation is exhibited in Fig. 6.

The initial (T_i) and maximum (T_{max}) temperatures of transition, which are presented in Table 4, showed no logical pattern with respect to the physicochemical characteristics of the bitumens studied. However, a significant correlation was again found between the final temperature (T_f) of transition (in nitrogen gas) and the corresponding total sulfur content of the bitumens studied and as shown in Fig. 6, i.e., BK bitumen with the lowest T_f value of 625°C possessed the lowest total sulfur content of 4%, while Y bitumen containing 8% sulfur had a T_f value of 725°C.

There was no logical pattern to the thermal data presented with respect to the metal contents (Ni,V) of the bitumens.

The significant correlation presented between the total sulfur content of the bitumens studied and some of their thermal data, in addition to the distinguishable shapes of the different thermogravimetric curves, can be used for the purpose of their characterization and identification and consequently as a fingerprint.

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