A STUDY OF ASPHALTIC CEMENTS AND THEIR FRACTIONS BY THERMOGRAVIMETRY

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ABSTRACT

Thermal degradation of a number of asphaltic cements and their fractions has been studied using thermogravimetry (TG). It was found that TG can be used to characterise each asphalt and detect changes in the original crude oil or the processing conditions. Also an estimate of the asphaltene content may be obtained by either a multiple regression equation or a simple correlation between the amount of asphaltenes in an asphalt and the mass loss in the temperature range 410–500°C.

INTRODUCTION

In the past, thermogravimetry has been used to characterise a selection of fuel oils [1]. More recently this work was expanded to study heavy fuel oils and their separated fractions (viz. paraffins, aromatics, polar materials and asphaltenes) under burning and pyrolysis conditions [2]. Thermogravimetry is an appealing method of analysis because of the ease and speed of its application, hence, work was performed to determine its potential for characterising asphaltic cements. In the present project the thermal decomposition parameters of a number of asphalts and their separated fractions are studied, and it is shown that thermogravimetry may be used to detect changes in the original crude oil or the processing conditions. Also, it is found that an estimate of the asphaltene content may be obtained by TG for "straight-run" and "air-blown" asphaltic cements.

EXPERIMENTAL

Separation of asphalt

A sample of each asphaltic cement used was separated into four generic fractions, termed asphaltenes, saturates, naphthene-aromatics and polar-aromatics, by a standard procedure [3].

TABLE 1

Compositional analysis and penetration range of asphalts

Asphalt sample	Penetration range [4] (0.1 mm/5 s/100 g/25°C)	Mass %			
		Saturates	Naphthene-aromatics	Polar-aromatics	Asphaltenes
A	180–200	13.5	45.7	35.4	5.4
B	180–200	15.1	39.1	35.2	10.6
C	180–200	11.3	49.9	25.2	13.6
D	80–100	7.1	45.2	32.4	15.3
E	40–50	12.9	49.1	16.2	21.8
F	12–25	17.4	31.9	22.6	28.1

The asphaltenes are the most polar fraction and are separated by their insolubility in n-heptane. The soluble remainder (petrolenes) is absorbed on a chromatographic column and sequentially desorbed with solvents of increasing polarity. Successive eluate cuts are taken to yield the other three fractions. The results of this separation and the penetration range for each asphalt are shown in Table 1.

Samples C and E were from the same crude oil but sample C is a "straight-run" product whereas sample E has been processed further by air blowing at elevated temperatures. The remainder of the samples were all from different sources.

Thermal analysis

The thermal analyses were performed on a Mettler TG 50. Each sample (10 ± 2 mg) was placed in a platinum crucible inside the thermobalance and heated to 650°C at 10°C min^{-1} in an air flow of 200 ml min^{-1}. Each sample was placed in the crucible unprocessed except the asphaltenes which were ground to < 150 μm before testing.

It was found that the thermal breakdown parameters for each asphalt were dependent on the crucible material, and that very different results were obtained when alumina and silica crucibles were used.

RESULTS AND DISCUSSION

Each of the asphalt samples and their separated fractions were analysed by thermogravimetry; the derivatives were automatically determined simultaneously. The DTG curves of the asphalts are shown in Fig. 1A–F. Although each asphalt produced its own characteristic DTG curve, each degraded in four major stages in the temperature ranges 190–370, 370–410,
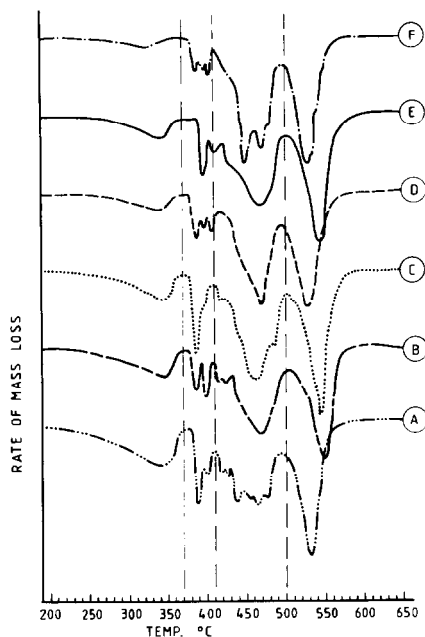
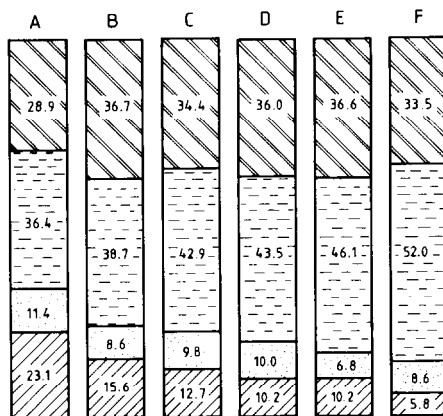Fig. 1. DTG curves of asphaltic cements.

Fig. 2. Percent mass loss in four temperature ranges for asphaltic cements. ▨ First temperature range, TR1 (190–370°C); ▤ second temperature range, TR2 (370–410°C); ▥ third temperature range, TR3 (410–500°C); ▨ fourth temperature range, TR4 (500–650°C).

410–500 and 500–650°C. The mass loss data in these temperature ranges are shown in Fig. 2. From Figs. 1 and 2 it can be seen that each asphalt has characteristic thermal breakdown parameters which may be used to identify it, and detect any changes that have taken place either in the crude oil or, as shown by samples C and E, the processing conditions.

The DTG curves of the saturate fractions are shown in Fig. 3. The maximum rate of mass loss is at about 340°C for each of the samples. From Fig. 4 it can be seen that the bulk of the mass (> 65%) was lost in the first temperature region for all the saturate samples. Each of the saturate fractions yielded a very similar thermal breakdown pattern, regardless of the origin.

The results for the naphthene-aromatic fractions are shown in Figs. 5 and 6. In each case this fraction loses mass rather evenly over the four temperature ranges, but the differences between the thermal degradation patterns of this species are greater than for the saturate fraction.

The DTG curves of the polar-aromatic fraction are shown in Fig. 7. The maximum rate of mass loss is in the two upper temperature ranges for this fraction. From Fig. 8 it can be seen that the majority of the mass (> 85%) is lost above 410°C in each case. The polar-aromatic fractions also have similar combustion profiles to one another.
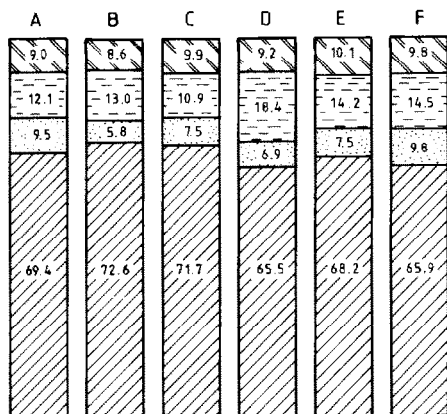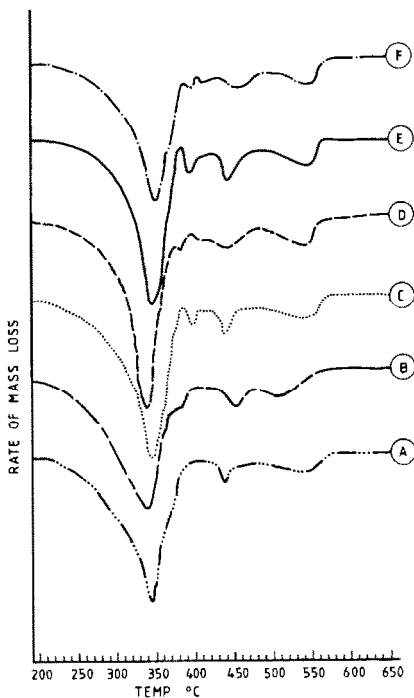
Fig. 3. DTG curves of saturate fractions.

Fig. 4. Percent mass loss in four temperature ranges for saturate fractions. For legend, see Fig. 2.

Fig. 9 displays the DTG curves of the asphaltene fractions. It can be seen that these species break down gradually in the lower temperature period and then suddenly decompose at a relatively fast rate. From Fig. 10 it can also be seen that the weight loss is very localised and that each asphaltene fraction loses at least 72% of its weight in the temperature range 410–500°C.

The average molecular weight of the asphaltene fraction as determined by classical methods such as ultracentrifugation [5], ebullioscope [6] and cryoscopy [7] has been reported to be higher than that of the whole asphalt. The asphaltenes are also the most polar species and according to Ciajolo and Barbella [2] the thermal decomposition is unaffected by oxygen. With this evidence it would be reasonable to expect the asphaltene fraction to decompose mainly in the higher temperature range (500–650°C), but this is not the case. This may be explained by the recent work performed by Boduszynski [8]. He found, by field ionisation mass spectroscopy, that the average molecular weights of the asphaltenes were in fact lower than those of the whole asphalt, and that intermolecular association is responsible for the erroneously high molecular weight values obtained by the classical methods.
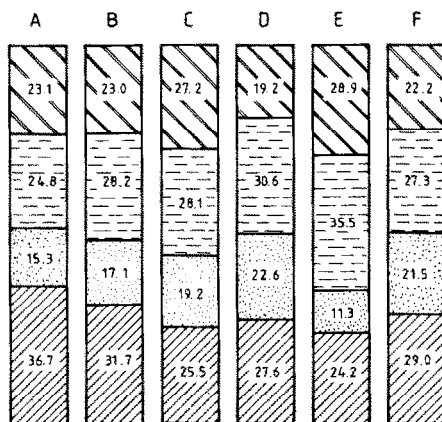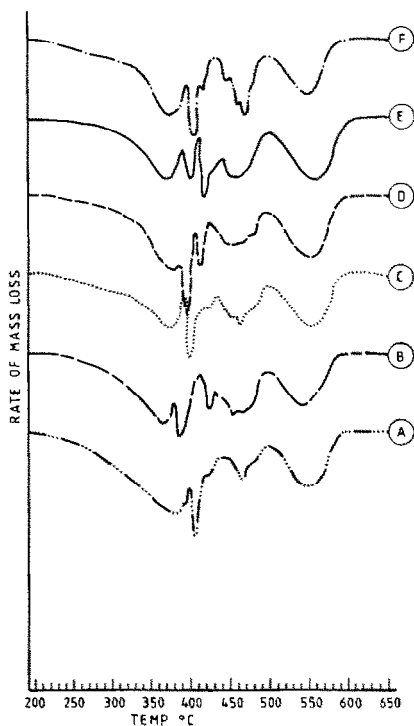
Fig. 5. DTG curves of naphthene-aromatic fractions.

Fig. 6. Percent mass loss in four temperature ranges for naphthene-aromatic fractions. For legend, see Fig. 2.

Studying the overall thermal breakdown characteristics of the separated fractions, it appears that each corresponding fraction degrades in a similar fashion regardless of the original asphalt. The mean values for the mass loss for each fraction in the four temperature ranges were calculated and from these values four equations were formulated to describe an average affect of each fraction on the mass loss of the complete asphalt in the various temperature regions:

Mass loss in TR1 (190–370°C) = $0.69S + 0.30N_a + 0.08A + 0.09P_a$

Mass loss in TR2 (370–410°C) = $0.09S + 0.18N_a + 0.07A + 0.06P_a$

Mass loss in TR3 (410–500°C) = $0.14S + 0.28N_a + 0.76A + 0.41P_a$

Mass loss in TR4 (500–650°C) = $0.08S + 0.24N_a + 0.09A + 0.43P_a$

TR = temperature range; S = mass % saturate; N_a = mass % napthene-aromatic; P_a = mass % polar-aromatic; A = mass % asphaltene.

If there is no interaction between fractions these equations should be able to predict the proportion of each fraction in an asphalt from the mass loss
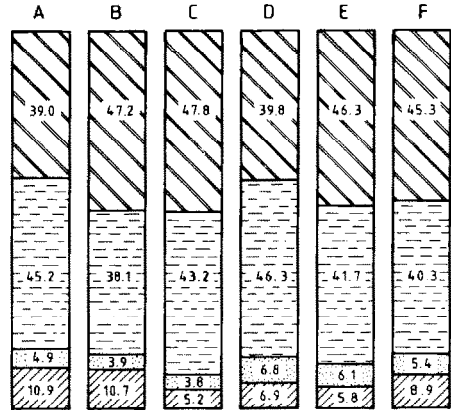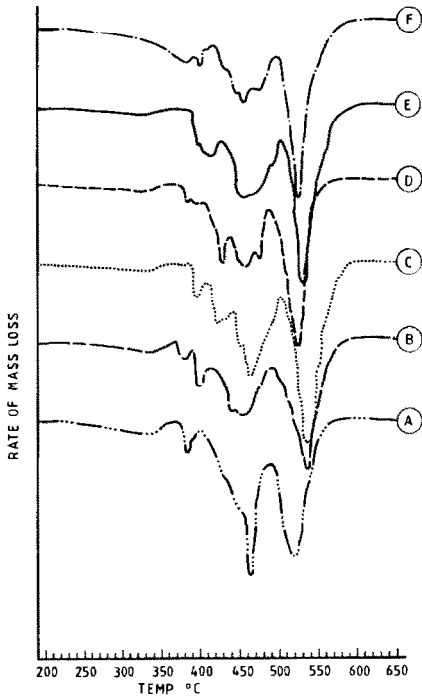
Fig. 7. DTG curves of polar-aromatic fractions.

Fig. 8. Percent mass loss in four temperature ranges for polar-aromatic fractions. For legend, see Fig. 2.

data in each temperature range and vice versa. The difference between the calculated and the actual mass losses in the four temperature ranges for each sample are shown in Table 2. It can be seen that (except for sample A) the differences are very large, strongly implying that there is an interaction between the various fractions.

As the asphaltene content increases from A to F (Table 1), so does the difference between the calculated and actual mass losses. A standard regression analysis technique [9] also found the asphaltenes to be the greatest contributor to the interaction.

The effect of this interaction seems to decrease the amount of mass lost in the first two temperature ranges with a consequent increase in the last two temperature regions. This could be caused by either physical inhibition or intermolecular association, or more likely a combination of these. The physical inhibition process would involve less reactive and lower volatile species blocking the easy access of oxygen and exit of volatiles. The intermolecular association would include secondary chemical bonding, such as Van der Waals forces, dipole–dipole interaction, hydrogen bonding, etc.
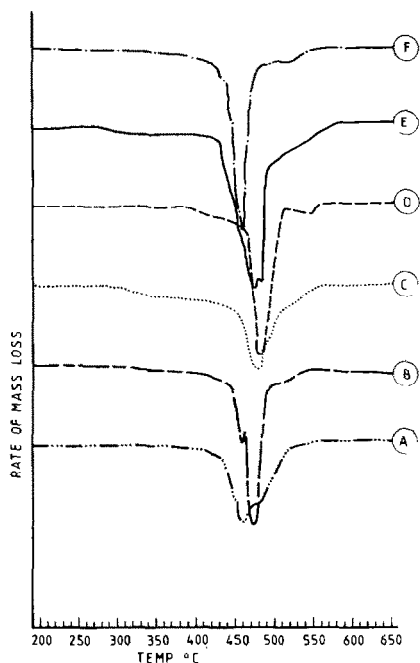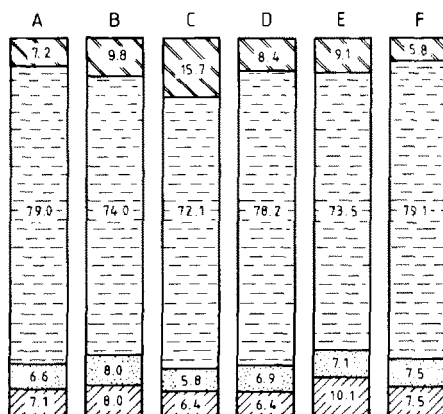
Fig. 9. DTC curves of asphaltene fractions.

Fig. 10. Percent mass loss in four temperature ranges for asphaltene fractions. For legend, see Fig. 2.

Another possible association could arise from the structure of the asphaltenes. It has been shown [10] that petroleum asphaltenes contain long, straight alkyl side-chains (C_{10} to C_{30}) connected to a polar block. These alkyl chains would preferentially dissolve in the alkane and cycloalkane species of asphalt, which would include the majority of the saturate fraction. Thus, the asphaltenes may be acting analogously to surfactants. If sufficient asphal-

TABLE 2

Difference between calculated and actual mass loss values

Sample	Δ Mass %			
	TR1	TR2	TR3	TR4
A	− 2.16	− 0.26	0.69	1.93
B	− 10.30	− 2.57	3.56	9.30
C	− 12.88	− 2.21	5.79	9.30
D	− 11.97	− 1.83	4.67	9.13
E	− 16.32	− 5.83	1.27	14.87
F	− 19.84	− 2.02	9.85	12.00

TABLE 3

Difference between calculated and actual compositions

Sample	$S\%$	$N_a\%$	$A\%$	$P_a\%$
A	−0.6	0.3	0.2	0.2
B	3.5	−8.3	0.3	4.5
C	−0.2	6.3	−1.0	−5.2
D	−2.1	1.6	0.4	0.1
E	−2.8	5.9	−0.1	−3.0
F	2.3	−5.8	0.3	3.2
Root mean sum of squares (RSS)	3.9	9.5	0.8	5.8

tenes exist, micelle formation may result, composed of non-polar hydrocarbons in the centre (mainly from the saturate fraction) surrounded by polar materials (from the asphaltenes). This would increase the resistance of the saturate fraction to oxidation and volatilisation.

Another set of equations was formulated taking into account the interaction between the fractions. These were inverted to obtain the proportion of each fraction from the mass loss in the four temperature regions:

$$S = 0.73M_1 - 1.52M_2 + 0.71M_3 - 0.38M_4$$
$$N_a = 0.64M_1 + 0.28M_2 - 0.03M_3 + 0.98M_4$$
$$P_a = 0.13M_1 + 3.64M_2 - 0.75M_3 + 0.83M_4$$
$$A = -0.24M_1 - 1.41M_2 + 1.05M_3 - 0.46M_4$$

M_1 = mass loss in TR1; M_2 = mass loss in TR2; M_3 = mass loss in TR3; M_4 = mass loss in TR4.

The difference between the observed results and those predicted from the above equations for the proportions of the fractions is shown in Table 3. From inspection of the residual and RSS values in Table 3 it can be seen that except for the asphaltenes the differences between the observed and predicted values are too large for practical use. In order to determine if a useable correlation between TG and the proportions S, N_a and P_a exists, further work is required. However, an estimate of the asphaltene content may be obtained from the multiple regression equation. A simple correlation was also found between the n-heptane asphaltene content and the mass loss in the third temperature range (410–500°C). The asphaltene contents of another four samples were determined in addition to the six samples already studied. The results from all ten samples are shown in Fig. 11. The data gave a good linear fit over the range studied with a squared regression correlation coefficient value of 0.98.

The asphaltene content has been found to have a large effect on the mechanical and rheological properties of asphalt [11–13] and there is also a
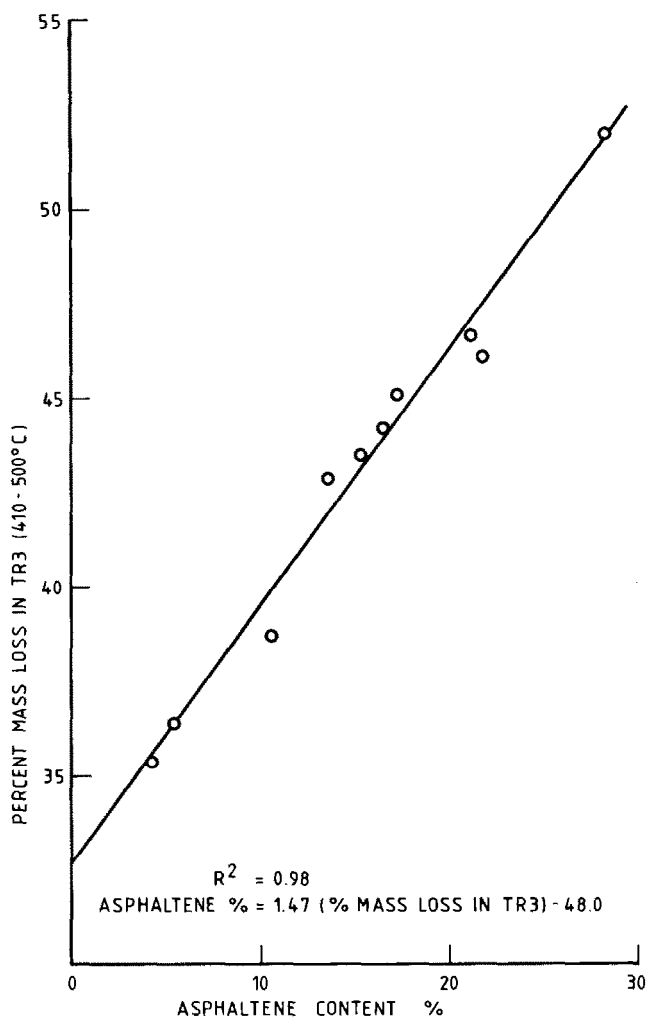
Fig. 11. Asphaltene content versus percentage mass loss in TR3.

link between the asphaltene content and the glass transition temperature [14]. Consequently, knowledge of the quantity of asphaltenes in an asphalt is often required. The time necessary to determine the asphaltene content by standard methods is in the order of one to two days. Using thermogravimetry an indicative result for the asphaltene content can be obtained in 1.5 h.

CONCLUSION

Thermogravimetry may be used to study "straight-run" and "air-blown" asphaltic cement to monitor changes occurring in either the crude or processing conditions.

Thermal analysis of the fractions separated from asphalt showed that each particular fraction degraded in a similar fashion, regardless of the original asphalt. However, the thermal breakdown of the complete asphalt differed significantly from the breakdown pattern calculated proportionally from the TG data of the separated fractions, indicating an interaction between the various fractions in the whole asphalt. The asphaltene fraction was found to be the major contributor to this interaction.

Even taking this interaction into account, the proportions of the fractions were not predicted accurately enough for practical purposes, from the thermal breakdown parameters. It was found, however, that an estimate of the asphaltene content could be obtained from either a multiple regression equation or more simply from a linear correlation between the asphaltene content and the mass loss in a certain temperature range.

In short, thermogravimetry can provide an extremely useful means of characterising asphaltic cements and rapidly estimating the asphaltene content simultaneously.

ACKNOWLEDGMENTS

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