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THERMOGRAVIMETRIC CHARACTERIZATION OF QUAYARAH HEAVY CRUDE OILS

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Five heavy crude oil samples from the Quayarah field were thermally evaluated using two modes of thermogravimetry (TG): dynamic and programmed TG with heating and hold-up periods at 350 and 550°. The light and medium volatility fraction ($L+M$) appeared directly proportional to the metal content. In contrast, the heavy fraction (H) (350–550°) was inversely proportional to the metal content. This contradiction was attributed to the autocatalytic degradation of some of the heavy fraction into lighter species, which upgrades the crude with respect to the ($L+M$) fraction at the expense of the heavy fraction. The crudes were identical with regard to the ratio ($L+M$) to ($H+R$), where R = residue, as a consequence of their identical API gravity and sulphur contents.

The rate of degradative volatilization of the heavy fraction was measured by DTG, which indicated a direct correlation with the vanadium content as regards the onset temperatures and the DTG peak maximum.

Heavy crude oils are rapidly gaining more attention, and their share in the total world production of petroleum is rapidly increasing. The study of their properties and their characterization and evaluation provide important data for the design of processes for their utilization; the availability of such data for crudes in discovered but unexploited oil fields determines their future potentials. The Quayarah oil field is located in the north of Iraq, south-west of the city of Mosul. Quayarah crude oil is produced in limited quantities and is used mainly to produce road asphalt.

Analytical methods make use of the different physicochemical properties of crude oils for their characterization. These include techniques such as API gravity, density, ASTM–IP distillation, gas and liquid chromatography, spectroscopy, etc.

Thermogravimetry (TG) has proved to be useful in distinguishing between crude oils [1], obtaining distillation curves [2], the characterization of crude oils of various API gravity [3], and the acquisition of important data in enhanced oil recovery studies [4].

In this research, programmed TG [3] and dynamic TG are used to characterize heavy crude oil samples from the Quayarah oil field. The data are correlated with

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some physicochemical parameters and the thermal curves are interpreted in terms of autocatalysis and induced cracking.

Experimental

The apparatures used was as reported earlier [3]. Samples: five heavy crude oil samples from Quayarah were used in this investigation. The relevant data on these crudes are presented in Table 1. Dynamic TG experiments were carried out under a

Table 1 Some characteristics of the studied crude oils

Oil	API	S, %[a]	V, ppm[b]
1	17.37	6.79	186
2	15.82	6.80	183
3	17.37	6.78	173
4	17.37	6.67	170
5	17.30	6.80	162

[a] determined according to IP method

[b] measured using flame atomic absorption spectrophotometry.

dynamic N_2 gas flow of 25 ml min^{-1} on samples weighing 5–10 mg at a heating rate of 100 deg min^{-1}. Derivative thermogravimetric (DTG) curves were recorded simultaneously.

Programmed TG: the samples were heated from ambient temperature up to 350° at a rate of 100 deg min^{-1}, and were held at this level for 2.5 min. Heating was then continued at the same rate up to 550°, where the temperature was again kept constant for 2 min.

Results and discussion

Programmed TG

The general profile of the curves of the analysed samples resembles that observed for light and medium crude oils [3] as indicated in Fig. 1. The quantitative evaluation of the curves is given in Table 2. It can be seen from Fig. 1 and Table 2 that heavy crude oils are distinguishable from each other because significant

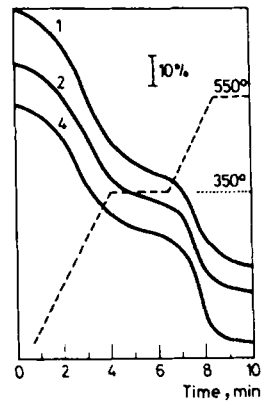

Fig. 1 Programmed TG curves of some heavy crude oils

Table 2 Quantitative evaluation of the programmed TG curves[a]

Oil	$L+M^b$, %	H^c, %	R, %	$(L+M)/(H+R)$
1	50.22	33.92	15.86	1.009
2	50.00	35.00	15.00	1.000
3	49.03	36.77	14.20	0.962
4	49.54	36.48	13.98	0.982
5	49.01	37.17	13.82	0.961

[a] average of 3 determinations
[b] weight loss from start till end of 350°C + hold
[c] weight loss from 350°C + hold to end of 550°C + hold

differences can arise in the heavy fraction and the percentage residue. The analyzed crudes, however, were almost identical in their light and medium fractions (weight loss up to the end of the hold interval at 350°). It is important that the weight loss up to 350° at the very beginning of the hold period varies for each crude and becomes higher, the higher the vanadium content of the crude (Fig. 2). The hold interval at 350° could decrease the slope of the dependence of the light and medium fraction on the vanadium content (Fig. 2). This can only be attributed to the action of vanadium in catalyzing [5] the low-temperature ($\leqslant 350°$) degradation of heavy cuts into light and medium cuts or the covolatilization of vanadium porphyrins with light and medium species [6]. This explanation may be confirmed by the decrease in the heavy fraction of the crude oils (loss from 350° up to the end of the hold time at 550°) with increasing vanadium content (Fig. 3). It can be seen from Fig. 3 that the heavy fraction and the residue are interdependent. While the residue percentage increases in a linear mode with the vanadium content, the heavy fraction decreases

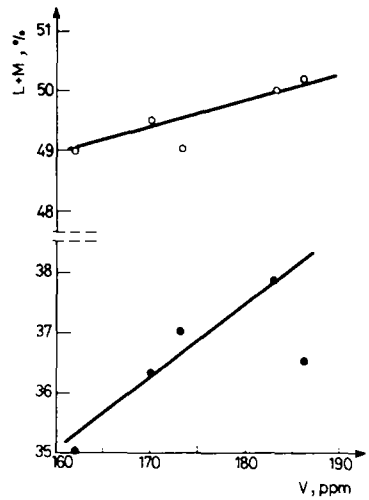

Fig. 2 Dependence of the $L+M$ fraction on the vanadium content: 0, weight loss upto 350 °C and 0, weight loss till the end of the hold interval at 350 °C

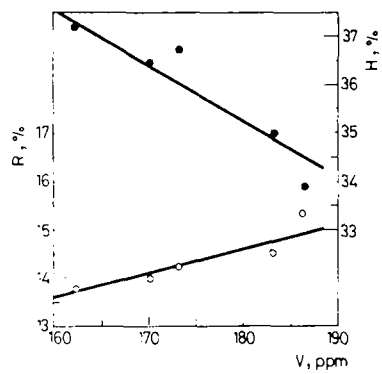

Fig. 3 Variation of the heavy fraction, H, and the residue, R with the vanadium content

in an opposite manner, so that the sum of the two is almost constant for the analysed crudes (50.6% ± 0.2).

For light and medium crude oils, the $L+M$ fraction decreased linearly with the percentage sulphur [3]. In the present case the similarity of the percentage sulphur (~6.8%) may be a mirror image of the identical ($L+M$) fraction values of the heavy crudes (~50.0%). However, some gaseous sulphur compounds, e.g. hydrogen sulphide, were noticed among the evolved gases during crude oil distillation [7].

The analysed crudes are characterized by almost identical API gravity values, which is consistent with the identical $(L+M)/(H+R)$ ratios (Table 2). The ratio

$(L+M)/(H+R)$, therefore, can be considered a significant datum for crude oils, in accordance with the previous findings [3].

Dynamic TG

While the profile of the TG curves of light oils is not significant, the heavy crude oils yielded TG curves with two distinct weight loss stages (Fig. 4). The DTG curves are more reliable in showing the qualitative sorting of the crudes, as concerns the

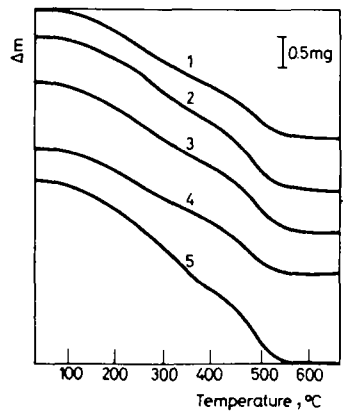

Fig. 4 Dynamic TG curves of heavy crude oils

initial weight loss temperature of the second stage and also the temperature at which the maximum rate of weight loss occurs (Fig. 5). Table 3 details the quantitative evaluation of the TG and DTG curves. During catalyzed combustion studies on the crude oils, the DTG curves were also more informative than the TG curves [4].

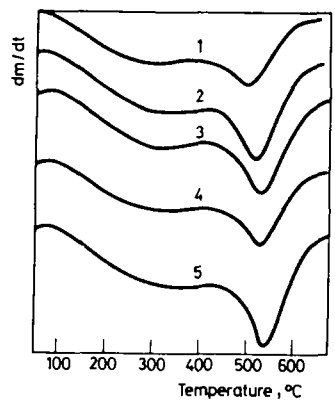

Fig. 5 Dynamic DTG curves of heavy crude oils

Table 3 Quantitative evaluation of dynamic TG curves

Crude	$(L+M)^a$, %	T_d^b, °C	DTG 2^c_{max}, °C
1	37.3	412	506
2	30.6	416	519
3	36.8	422	520
4	28.6	421	520
5	30.2	425	532

[a] weight loss from start till 350 °C

[b] initial decomposition temperature of the second stage

[c] temperature of the maximum rate of weight loss of the second stage

The autocatalysis of the vanadium species on the thermal behaviour of the heavy crude oils was visualized more clearly in the dynamic TG curves than in programmed TG plots. The temperature of the maximum rate of weight loss in the first stage was $<350°$, which was the lower, the higher the content of vanadium (Fig. 6). Therefore, the low-temperature ($\leqslant 350°$) weight loss part is not restricted to

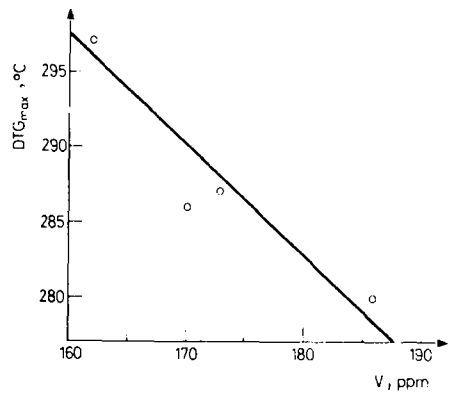

Fig. 6 Dependence of DTG 1 (temperature of maximum rate of weight loss in the first stage) on the vanadium content

distillation but to catalytic degradation. The second stage of weight loss starts beyond 400°. The initial decomposition temperature is dependent on the vanadium content. The higher the vanadium content, the lower the decomposition temperature (Fig. 7). The weight loss occurred in a temperature range at which asphaltenes [8] and heavy vacuum residue [9] decompose, 480–530°. Again, the DTG peak maximum DTG 2 decreased with the increase of the vanadium content.

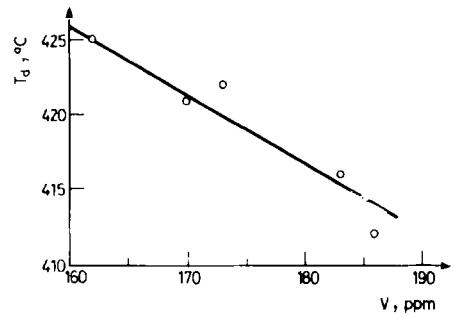

Fig. 7 Dependence of the initial decomposition temperature of the second stage with vanadium content

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Zusammenfassung Fünf vom Quayarah-Feld stammende schwere Rohöle wurden mittels dynamischer und programmierter TG mit konstanten Perioden bei 350 und 550 °C charakterisiert. Der Anteil der leicht- und mittelflüchtigen Fraktion ($L + M$) schien proportional, der der schwerflüchtigen Fraktion (H) (350 550°) dagegen umgekehrt proportional dem Metallgehalt zu sein. Dieser Widerspruch wurde dem autokatalytischen Abbau einiger der schwerflüchtigen Komponenten zu leichteren Spezies zugeschrieben, der zu einer Erhöhung des Anteils der ($L + M$)-Fraktion auf Kosten der schwerflüchtigen Fraktion führt. Die Rohöle waren wegen der gleichen API-Schwere und gleicher Schwefelgehalte hinsichtlich des Verhältnisses von ($L + M$) zu ($H + R$) identisch (R = Rückstand). Die Geschwindigkeit der degradativen Verflüchtigung der schweren Fraktion wurde mittels DTG gemessen, wobei sich eine direkte Korrelation zwischen dem Vanadingehalt einerseits und der Einsatztemperatur bzw. dem DTG-Peakmaximum andererseits ergab.

Резюме — Пять образцов тяжелой сырой нефти месторождения Кваярах были исследованы методами динамической термогравиметрии и термогравиметрии с программированным нагревом и периодами задержки при 350 и 550°. Образование легких и средних фракций ($Л + С$) было прямо пропорционально содержанию металла, тогда как количество тяжелой фракции ($Т$) (350–550°) — обратно пропорционально содержанию металла. Это противоречие было отнесено за счет автокаталитического распада некоторого количества тяжелой фракции на более легкие фракции, тем самым обогащая сырую нефть этими фракциями за счет тяжелой фракции. Все

образцы сырой нефти характеризовались одинаковым соотношением фракций $Л + С$ и $Т + О$, где $О$ – остаточная фракция, что являлось следствием их одинакового АПИ удельного веса и содержания серы. Скорость распада тяжелой фракции на более легкие была измерена методом ДТГ. Скорость распада, относительно начальных температур и максимумов ДТА пиков, коррелировалась с содержанием ванадия в данных образцах нефти.