

THERMAL ANALYSIS OF CRUDE OILS AND COMPARISON WITH SIMDIST AND TBP DISTILLATION DATA

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Abstract

Four commercial Saudi Arabian crude oils were characterized by thermogravimetry (TG) and differential thermal analysis (DTA). These crude oils, Arab Berri (AB), Arab Light (AL), Arab Medium (AM) and Arab Heavy (AH), were also subjected to the traditionally employed true boiling point (TBP) distillation and simulated distillation (SIMDIST). The TG/DTA data show that the hydrocarbons present in these crude oils fall into four groups: the volatiles, the low molecular weight, the medium molecular weight and the high molecular weight compounds. These four types of hydrocarbons were observed to display certain trends, such that the volatile and low molecular weight hydrocarbons increased, while the medium and high molecular weight hydrocarbons decreased with the lightness of the crude. The volatile contents of AB, AL, AM and AH crude oils up to 280°C were 50.1, 42.2, 42.3 and 38.5 mass percent, respectively. This confirms that AB is the lightest of these crude oils with maximum volatile content. The mass percentage loss from the TG results is in good agreement with the percentage distilled from TBP (ASTM D 2892) and SIMDIST. During evaporation, the TG mass loss follows a similar trend to those of the TBP and SIMDIST results and thus behaves like distillation. During the oxidative degradation, the TG curve shows a higher mass loss as compared to the distillation data. The higher deviation of the TG mass loss and percentage distilled at the higher-temperature end of the curve may be attributed to the higher content of asphaltene and carbonaceous material present in AH as compared to the AB crude oil. At around 200°C, the TG mass loss curve intersects the TBP and SIMDIST curves and shows a derivation from distillation behaviour. This intersection temperature of the TG and distillation curves is observed to decrease with the heaviness of the crude and can be an indication of the onset of thermal degradation of hydrocarbons present in the crude oil. On the whole, the TG data closely resemble the distillation results.

Keywords: DTA, DTG, Saudi Arabian crude oils, SIMDIST, TBP distillation, TG

Introduction

Crude oils and other complex materials are characterized by a number of physical and chemical analytical parameters. These include viscosity, pour

point, carbon residue and solvent insolubles. To achieve a more in-depth analysis, these materials are fractionated into a number of cuts and characterized by a combination of physico-chemical analytical techniques. Thermogravimetry (TG) is one of the techniques that allows a study of the thermo-oxidation and mass loss of crude oils over an extended temperature range. All crude oils undergo mass loss on heating, but it is possible to differentiate between two crude oils on the basis of the characteristic shapes of their TG curves.

A number of analytical methods have been applied to crude oils and petroleum products in order to determine their properties. These include simulated distillation (SIMDIST) by gas chromatography [1, 2], pyrolysis gas chromatography [3], capillary gas chromatography [4, 5], mass spectrometry [6], gas chromatography – mass spectrometry [5, 7, 8], infrared spectroscopy [9] and atomic absorption spectrometry [10].

TG has been used extensively to study the characteristic of crude oils and other petroleum products. Bae published a design for a high-pressure thermobalance [11] and demonstrated the application of TG for determination of the fire flooding conditions characteristic of crude oils [12]. Masek investigated heavy tar fractions by TG [13] and studied the effect of the purge gas composition on the TG results of fuel oils [14]. Lubricating oils have also been studied by TG by Hsu and Cummings [15], who developed a method of determining the oxidative-autoignition characteristics of heat transfer oil [16]. Dyszel [17] developed a TG method to distinguish Alaskan crude oil from other crude oils of the world. A number of investigators have used TG to characterize asphalt and bituminous material [18], heavy crudes and residue [19], petroleum distillates [20, 21] and asphaltenes [22] and to monitor the reaction between a crude oil derivative and sulfur [23]. Fischer demonstrated the applicability of TG for the microdistillation of petroleum and the quantification of asphaltic contents [24]. Barbooti *et al.* [25] used TG to characterize heavy crude oils.

This paper describes the utilization of TG/DTA methods to characterize Saudi Arabian crude oils, to further investigate the properties of the volatile components of these crudes and to correlate the characteristics with the thermo-oxidation behaviour of such crudes. The results of TG/DTA analysis were also correlated with true boiling point (TBP) distillation and SIMDIST data.

Experimental

Sample definition

The four Saudi Arabian crude oils for this study were supplied by Saudi Aramco. They were Arabian Berri (AB), Arabian Light (AL), Arabian Medium (AM) and Arabian Heavy (AH). These crude oils were stabilized at lower temperature before distillation. AH is produced from an offshore oilfield, Safania, located about 125 miles north-west of the exporting terminal Ras Tanura; this is

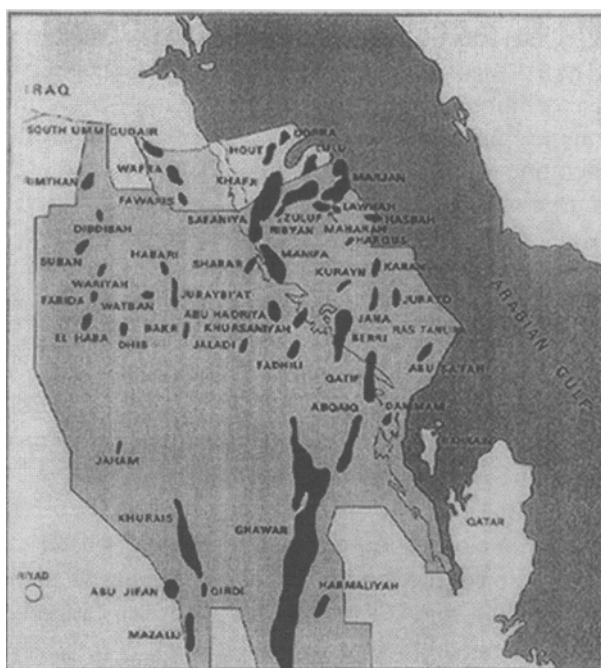


Fig. 1 Map showing the location of oil fields producing the Saudi crude oils under study

the world's largest offshore oil field. AM is produced from a blend of oils from the Abu Safah, Khursaniyah, Marjan and Zuluf oil fields. AL is a blend of products from the Abqaiq Ain Dar, Shedgum Uthmaniyah, Abu Hadriyah and Hawiyah oil fields. AB is produced from the Berri oil fields. A map showing the location of these oil fields is given in Fig. 1.

Thermal analysis

The equipment used for thermal analysis was a simultaneous thermal analyser STA-429 manufactured by Netzsch, Germany, which performs TG and DTA simultaneously. About 100 mg of crude oil was taken, with alumina as a reference material. The temperature was raised at a uniform rate of $10^{\circ}\text{C min}^{-1}$ from room temperature up to 1200°C in air atmosphere. In the thermal curves, the percentage mass loss, the differential temperature and temperature are plotted simultaneously.

DTA is a technique for measuring the amount of heat evolved or absorbed and the temperature at which these changes take place within the material. The temperature difference between a test sample and the reference material is measured as a function of temperature, while the substance and the reference material are

subjected to controlled temperature heating. A number of phenomena such as decomposition and oxidation may take place in a material when it is heated at a constant rate. TG is a technique in which the change in mass of a substance is measured as a function of temperature while it is subjected to controlled heating. The characteristic decomposition phenomenon is the appearance of an endothermic peak in a DTA curve with a corresponding mass loss. Oxidative degradation is characterized by an exothermic peak with corresponding mass loss.

Gas chromatographic simulated distillation (SIMDIST)

The system used for SIMDIST consisted of an HP 5880A gas chromatograph equipped with an FID and automatic sampler HP 7673A. The column employed was the UCW-982. The system was calibrated by analysing a mixture of normal paraffins from nC_5 to nC_{40} covering the temperature range from 36 to 525°C. The program used the boiling points of the paraffins and their corresponding retention times to produce a calibration curve. This curve is used to determine the boiling range distribution of the sample. A known amount of an internal standard consisting of C_{14} , C_{15} , C_{16} and C_{17} normal paraffins was added to the crude oil sample to calculate the percentage recovery and boiling range distribution up to 525°C. The program calculated the data and produced a SIMDIST report as percentage distilled vs. temperature. The detailed SIMDIST operating conditions and procedure are given elsewhere [1].

True boiling point (TBP) distillation

The TBP distillation data were obtained by using a computerized Gecil Distel 2892 apparatus having a column equivalent to 16 theoretical plates and operated at a reflux ratio of 5:1. This instrument is equipped with an electronic pressure sensor, a photoelectric level follower to measure the volume of distillate and distillation rate, a fraction collector with 12 distillate receivers, a vacuum pump and a refrigeration unit. Following the debutanization of crude oil at 25°C, the distillation was carried out under atmospheric pressure up to 200°C. Above 200°C, sufficient vacuum was applied to the system to keep the atmospheric equivalent temperature (AET) below 200°C, so that the cracking of hydrocarbons can be prevented. The TBP distillation was carried out up to 390°C. The vacuum distillation was performed by using a computerized Gecil Minidist 1160 apparatus in accordance with ASTM method D 1160. The vacuum distillation was carried out on the residue of TBP distillation and was continued up to 600°C AET. The system was operated at 2 mm Hg pressure. The detailed TBP experimental conditions and procedure are given elsewhere [1].

Results and discussion

Some of the properties of the Saudi Arabian crude oils used in this study are given in Table 1. These are API gravity, sulfur, nickel and vanadium contents. A very clear trend can be observed in these crude oils: the sulfur, nickel and vanadium contents increase with decrease in the API gravity. The reason for the decrease in the API gravity or the increased density of a crude oil is the increased asphaltene content. Asphaltenes are high molecular weight (high density) condensed aromatic and naphthenic systems containing sulfur linkages and aromatic sulfur groups such as thiophene and its benzene homologues. The heavy crudes also contain higher amounts of organometallic compounds called porphyrins, having nickel and vanadium central atoms attached to the nitrogen atoms of pyrrole-type rings [26]. Therefore, the higher the amount of asphaltenes and porphyrins, the higher will be the sulfur, vanadium and nickel contents and thus, the lower will be the API gravity of that crude oil.

Table 1 Some characteristics of Saudi crude oils under study

Crude oil	API Gravity	Sulfur/ wt%	Nickel/ ppm	Vanadium/ ppm
Arab Berri	38.60	1.20	0.6	2.2
Arab Light	33.45	1.98	3.2	15.5
Arab Medium	30.36	2.45	8.4	27.9
Arab Heavy	28.00	2.67	16.7	57.9

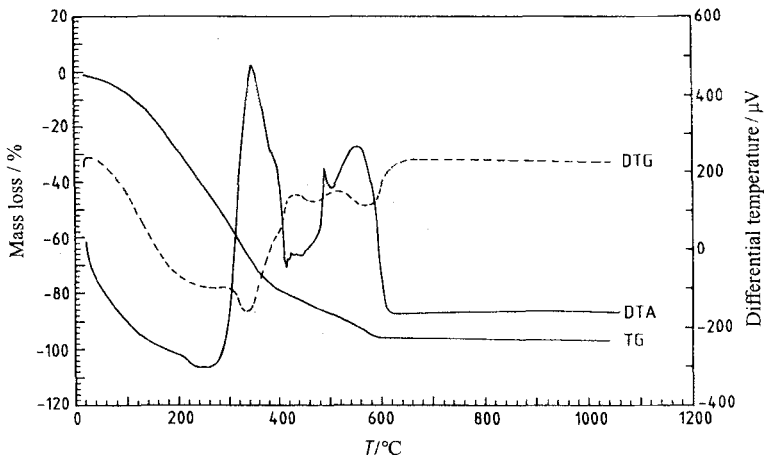


Fig. 2 TG, DTA and DTG curves of Arab Berri crude oil

TG, DTG and DTA curves of the AB, AL, AM and AH crude oils are shown in Figs 2 to 5. These curves demonstrate the following four regions of thermal effects:

Region 1: 20–280°C Region 2: 280–400°C

Region 3: 400–510°C Region 4: 510–620°C

Corresponding weight losses and maxima of endothermic and exothermic peaks for these four temperature ranges are presented in Table 2. In region 1, the mass loss of free moisture and volatiles hydrocarbons takes place in an endothermic reaction, since it is by evaporation. In the other three regions, the mass loss is accompanied by corresponding exothermic peaks. This effect is due to the oxidative degradation of different classes of hydrocarbons.

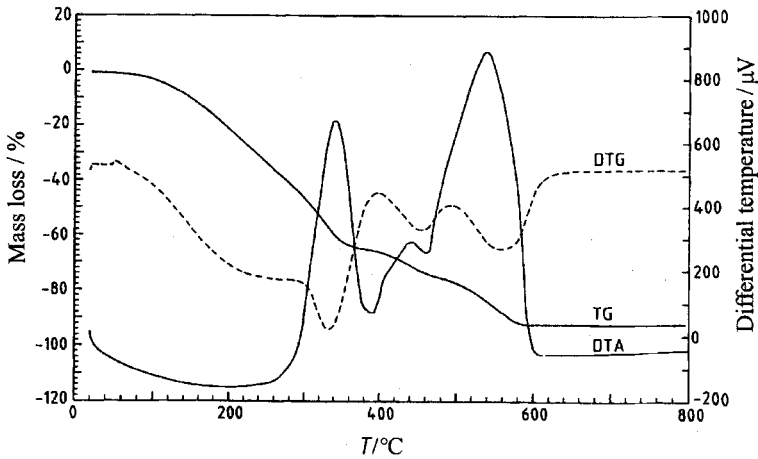


Fig. 3 TG, DTA and DTG curves of Arab Light crude oil

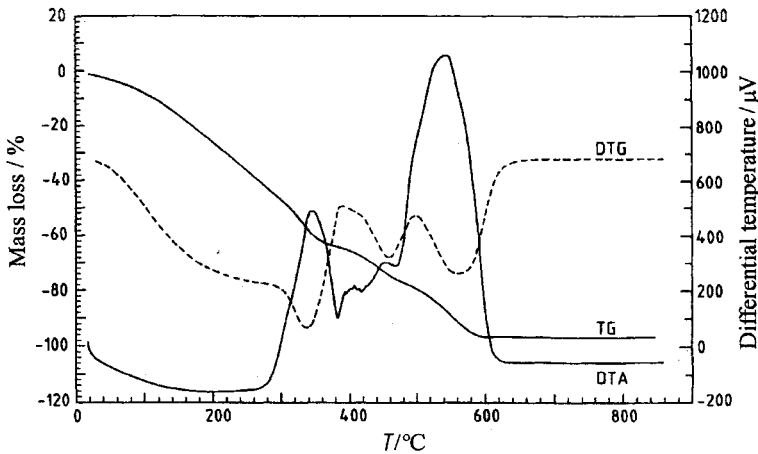


Fig. 4 TG, DTA and DTG curves of Arab Medium crude oil

The mass loss in the temperature range 20–280°C indicates the evaporative loss of free moisture and volatile hydrocarbons. The volatile contents of the crude oils increase with the lightness of the crudes (Fig. 6). The crude oils under

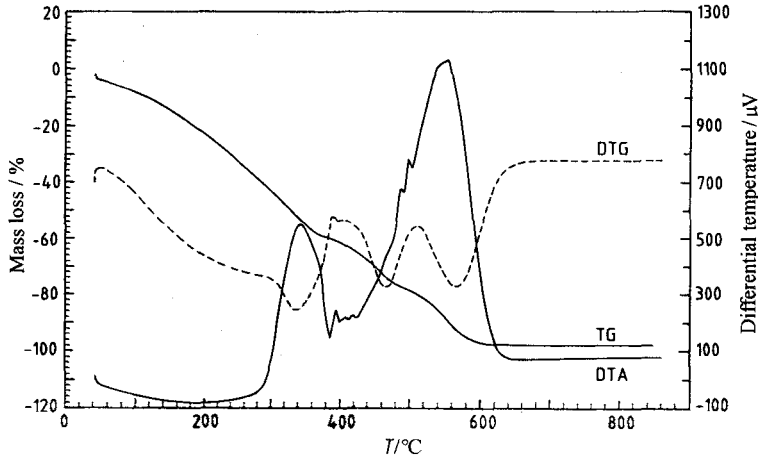


Fig. 5 TG, DTA and DTG curves of Arab Heavy crude oil

Table 2 TG mass losses for Saudi crude oils in four different temperature ranges

Crude oil	$T_{\text{range}}/^{\circ}\text{C}$	Mass loss/%	Maxima	$T_{\text{Thermal effect}}/^{\circ}\text{C}$
Arab Berri	20–280	50.1	–	–
	280–400	29.4	340	exo
	400–510	7.8	490	exo
	510–620	8.5	550	exo
Arab Light	20–280	42.3	–	–
	280–400	25.0	340	exo
	400–510	11.1	440	exo
	510–620	14.9	540	exo
Arab Medium	20–280	42.2	–	–
	280–400	23.3	350	exo
	400–510	13.7	450	exo
	510–620	17.4	550	exo
Arab Heavy	20–280	38.5	–	–
	280–400	24.0	340, 390	exo
	400–510	18.5	490, 500	exo
	510–620	17.4	550	exo

study have a trend such that AB is the lightest, while AH is the heaviest. Fifty percent of AB consist of volatiles, while AH contains 38.5% and it is 21% less light than AB. The volatile contents of AL and AM are 42.2 and 42.3%, respectively.

In region 2, in the temperature range 280–400°C, low molecular weight hydrocarbons are oxidized by the exothermic reactions. The mass percentage of these compounds in these crude oils again shows a trend, increasing with the lightness of the crude. AH contains 24.0%, AB 29.4%, and AM and AL 23.4 and

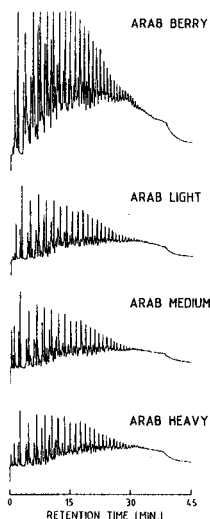


Fig. 6 Gas chromatograms obtained from simulated distillation of Arab Berri, Arab Light, Arab Medium and Arab Heavy crude oils

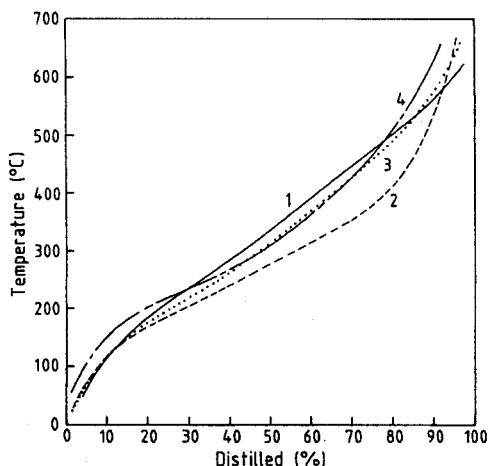


Fig. 7 A comparison of the SIMDIST behaviour of Four Saudi Arabian crude oils

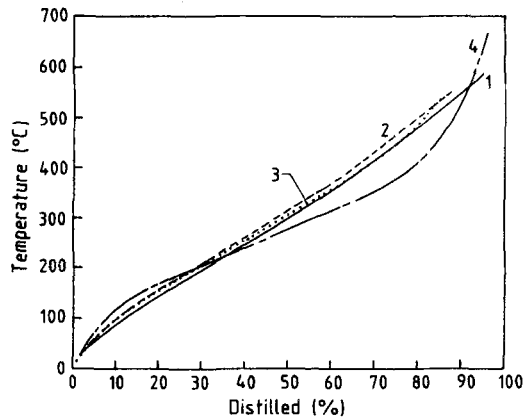


Fig. 8 Distillation behaviour of Arab Berri crude oil. (1) TBP volume percentage, (2) TBP mass percentage, (3) SIMDIST curve and (4) TG mass percentage

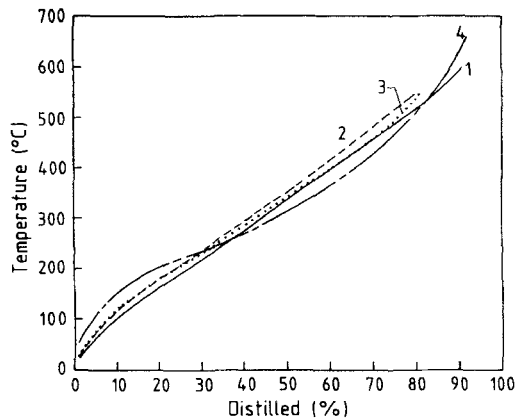


Fig. 9 Distillation behaviour of Arab Light crude oil. (1) TBP volume percentage, (2) TBP mass percentage, (3) SIMDIST curve and (4) TG mass percentage

25.1%, respectively. However, the curves of AH show an extra exothermic peak at 390°C, which indicates that AH contains two different types of low molecular weight hydrocarbons.

In region 3, in the temperature range 400–510°C, medium molecular weight hydrocarbons undergo oxidative degradation and the percentage mass loss decreases from AH to AB through the AM and AL crude oils. The amount of medium molecular weight compounds in AH was found to be 24% and it decreased proportionally with the lightness of the crude oil. The AB crude contained 7.8% of such medium molecular weight compounds. In this region, AH shows two exothermic peaks, at 490 and 500°C. AM and AL exhibit one peak, at 450°C, and

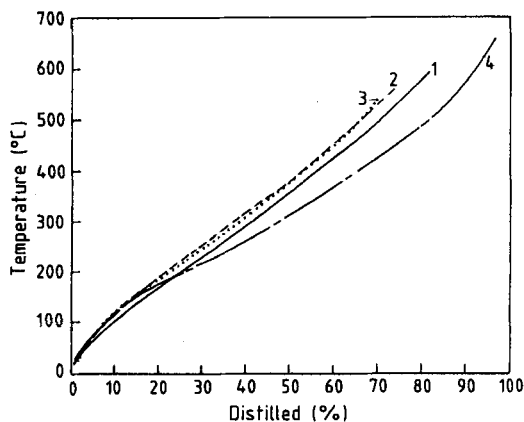


Fig. 10 Distillation behaviour of Arab Medium crude oil. (1) TBP volume percentage, (2) TBP mass percentage, (3) SIMDIST curve and (4) TG mass percentage

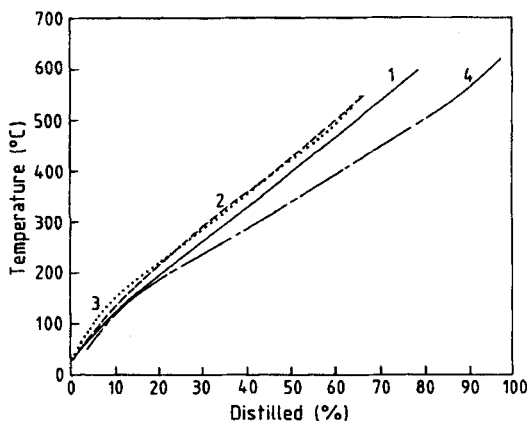


Fig. 11 Distillation behaviour of Arab Heavy crude oil. (1) TBP volume percentage, (2) TBP mass percentage, (3) SIMDIST curve and (4) TG mass percentage

AB shows an exothermic peak at 490°C. Analysis of region 3 indicates the presence of two different types of medium molecular weight hydrocarbons in AH. One of these types of compounds is also present in AB. The AM and AL crudes contain a type of hydrocarbons different from those of AH and AB.

High molecular weight compounds were oxidized in the region 510–620°C in all of the four crudes, characterized by exothermic maxima at 550°C, indicating that the crudes contain the same type of high molecular weight compounds. These high molecular weight hydrocarbons decrease from AH (17.4 wt%) to AB (8.5 wt%) through the AM (17.4 wt%) and AL (14.9 wt%) crude oils.

Comparison of TG data with TBP and SIMDIST results

The gas chromatograms obtained from SIMDIST of all the Saudi crude oils are shown in Fig. 6. The distillation results for all four Saudi crudes were plotted together with the TG mass percentage loss data and are illustrated in Figs 7 to 11. The comparison shows that up to 200°C the TG mass loss of all crudes behaves approximately as distillation and follows a similar trend to those of the TBP mass and volume percentage data and the SIMDIST results. The TG data show a lower mass loss up to 200°C as compared with the percentage distillation for the AB and AL crude oils. For AM, the TG data follows the TBP mass percentage and the SIMDIST curve up to 150°C and then a comparatively higher mass loss. For AH, the TG curve follows the TBP volume percentage trend up to 160°C and then moves towards a higher mass loss than the distillation data. The reason for the higher mass loss was that the crude was not only evaporated above 200°C, but also experienced oxidative degradation.

This difference in TG mass loss and percentage distilled in TBP and SIMDIST is observed to be higher at the high-temperature end of the curve as compared to the lower-temperature end. This is because, as the temperature progresses, the rate of distillation decreases, whereas in the case of TG, the rate of mass loss is higher due to oxidative degradation of the material. For the AH and AM crude oils, the difference between the percentage distilled and the TG mass loss is higher as compared to AL and AB. This phenomenon is attributed to the higher content of asphaltenes and carbonaceous material in heavy crudes as compared to light crude. The shape of the TG curve is also important: it is straighter for AH than for the other crudes, especially AB. A correlation will be developed between the TG mass loss and the distillation data after obtaining results for more crude oils. The temperature at which the TG curve of a crude intersects with the distillation curve may also serve as an indication of the temperature at which the thermal degradation can occur in the distillation of a crude. This intersection temperature is observed to decrease with the heaviness of the crude. This temperature is 250°C for AL as compared to 150°C for the AH crude oil.

Conclusions

The thermal analysis data show that the hydrocarbons of a crude oil can be classified into four types; the volatiles, the low molecular weight, the medium molecular weight and the high molecular weight hydrocarbons. The volatiles are characterized by heat absorption reactions leading to evaporation of these hydrocarbons. The other three types of hydrocarbons are identified by the presence of exothermic peaks in the DTA curve as a result of oxidative degradation of these hydrocarbons. The volatile contents of these crude oils were found to display a

trend: the lighter crude contains more volatiles as compared to the heavier crude. AH contains 38.5% volatiles, while AB has 50%. The volatile contents of AL and AM are each 42.0%. The mass percentage of low molecular weight hydrocarbons in these crude oils again shows a trend: it increases with the lightness of the crude. The medium and high molecular weight hydrocarbons were found to decrease with the lightness of the crudes and exhibit a trend from AH to AB through AM and AL.

The comparison of the TG mass percentage loss data with the TBP distillation and SIMDIST results shows that up to 250°C, the TG mass loss of the crudes behaves approximately as distillation and follows a similar trend to those of the TBP and SIMDIST results. This is because, at around 200°C, the volatiles and free moistures are evaporated and no thermal degradation of the crude occurs. At temperatures above 250°C, the TG curve shows a higher mass loss as compared to the distillation data. The reason for the higher mass loss is that the crude not only evaporates above 200°C, but also experiences oxidative degradation. The higher difference in TG mass loss and percentage distilled in TBP and SIMDIST at the high-temperature end of the curve as compared to the lower-temperature end indicates that, as the temperature elevation progresses, the rate of distillation decreases, whereas the rate of TG mass loss increases due to oxidative degradation of the material. The higher deviation of the TG mass loss and the percentage distilled at the higher-temperature end may be attributed to the higher content of asphaltenes and carbonaceous material in heavy crudes as compared to light ones. The temperature of intersection of the TG and distillation curves is observed to decrease with the heaviness of the crude, and can indicate the thermal degradation temperature limit of a crude oil.

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