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A new quick method of determining the group hydrocarbon composition of crude oils and oil heavy residues based on their oxidative distillation (cracking) as monitored by differential scanning calorimetry and thermogravimetry

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Abstract

A calorimetric-thermogravimetric method is described of determining mass percent contents of distillate fractions, paraffins, base oils, resins, asphaltenes and carbines in various crude oils. The method is based on recording DSC curves of a 10–15 mg sample heated in air in a calorimetric-cell at a rate of 40–50 °C/min. Additionally, weight loss of sample is found at temperatures before and after the reaction. At temperatures from 220 °C or higher distillation of the hydrocarbon mixture starts to be accompanied by its exothermic oxidation, thereby making possible monitoring the distillation (oxidation) of consecutive HC fractions by simple calorimetric-techniques. Differential scanning calorimeter "Thermodat" of high-calorimetric-resolution and sensitivity equipped with dedicated software was used for conducting the experiments and performing all the calculations. Percent contents of the main constituents in a number of heavy and light crude oils were determined and formulas for establishing paraffinic, base oil and coke-forming potentials of crude oils and oil residues derived. One full analysis of a sample takes no longer than 1.0–1.5 h. The method can be used for on-line quality control of various petroleum products, such as atmospheric and vacuum oil residues, cracking residues, lubricants, ceresins and paraffins.

Keywords: Crude oils; Fractional analysis; Paraffinonaphthenes; Differential scanning calorimetry

1. Introduction

Knowledge of the chemical composition of various crude oils and petroleum heavy residues is indispensable for correct product quality assessment and choice of optimal petroleum processing technologies. To obtain such knowledge one needs methods, preferably rapid, sufficiently accurate, easy to use and capable of performing on-line in industrial conditions. The known methods of chemical analysis employing selective solvent separation and extraction are labor, time consuming and thus do not meet the said requirements. Therefore, attempts are being constantly made to develop rapid instrumental methods of chemical analysis of petroleum products, among which those employing the principles of scanning calorimetry and thermogravimetry seem to be the most promising.

The majority of the work using these methods is directed towards elucidation of the nature of thermal reactions in the sample heated in the range 20–700 °C, finding the correlation between the chemical composition of the sample and its thermal behavior (properties) and establishing the influence of experimental conditions on the results obtained. Ranjbar and Push [1] studied the effect of the oil composition on the oil pyrolysis and combustion kinetics. Yoshiki and Phillips [2] studied kinetics of low-temperature oxidation and high-temperature cracking of Athabasca bitumen and its dependence on atmosphere, pressure, heating rate and support material. Laux et al. [3] investigated atmospheric, vacuum and visbreaking crude oil residues and their mixtures with and without dispersing agents by TGA at three different heating rates with a view to establish the correlation between the thermal and physico-chemical stability of these

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complex mixtures. Goncalves et al. studied crude oil asphaltenes and the coke by TG-DTA/GC/MS methods. Kök and Iscan [4] applied DSC to study crude oil combustion in the presence and absence of metal chlorides. Three different reaction regions were identified as low-temperature oxidation, fuel deposition and high-temperature oxidation in all the samples studied. Kök and Karacan [5] studied six light and heavy crude oils containing different amounts of saturate and aromatic (resin and asphaltene) fractions. The oils show two regions of weight loss—the low-temperature one, more pronounced for the lighter crudes, due to distillation of saturate fractions and the second one, beginning from ca. 400 °C, due to visbreaking and cracking of the heavy aromatic fractions remaining in the sample after evaporation of the lighter fractions. In [6] two Turkish crude oils were separated into their saturate, aromatic, resin and asphaltene (SARA) constituents and combustion experiments were carried out on whole crude oils and their fractions by TG/DTG. Temperature intervals and kinetic parameters of evaporation and oxidation of each fraction were determined. In [7] it was shown that the pyrolysis behavior of crude oils and their SARA fractions depends on the chemical nature of the constituents and that “each fraction in whole crude oil follows its own reaction (distillation and cracking) pathway independent of the presence of other fractions”. This important property of petroleum hydrocarbons is made full use of in the approach developed in the present paper.

It can be concluded from the above that some basic thermal properties of petroleum hydrocarbons and their natural mixtures, e.g. crude oils, have been well established. What is lacking is a more detailed, more quantitative assessment of the group hydrocarbon composition of crude oils and their heavy products. To attain this aim, new experimental approaches, new instruments with higher calorimetric-resolution and sensitivity than the conventional ones are needed. The author’s differential scanning calorimeter “Thermodat” meeting the said requirements was used for the present study. The instrument is the further development of the quantitative differential thermal analysis apparatus described in the author’s earlier publications [8–12].

2. Experimental

In the Thermodat set up two thin-walled (0.2 mm) stainless steel crucibles 4.5 mm in outer diameter and 4.0 mm in height are used, one for the sample and the other for the reference material (silver). The crucibles are put on the tips (hot junctions) of a chromel–alumel differential thermocouple and placed in a vertical tube furnace with open lower and upper ends to ensure good furnace ventilation. Samples of lubricants (4–6 mg) or crude oils (12–15 mg) in a crucible of said dimensions form a thin-layer and evaporate on heating without boiling (without forming bubbles). Due to good convection, the vapors and gases escape from the sample surface without the need to overcome atmospheric pressure (as in bubbles) and this is equivalent to conditions of distillation under reduced pressure. Besides, rapid removal of gaseous oxidation products and unobstructed supply of air (oxygen) to the sample ensure full oxidation of its constituents and minimal formation in it of condensation products (resins), which is a sine qua non condition for obtaining reliable experimental data.

Experiments were conducted in static atmosphere (air) and heating rates of 45–50 °C/min were commonly used. Heat effects ΔH, J of thermal reactions were calculated using the formula

$$-\Delta H = KA_t \tag{1}$$

where K is the heat transfer coefficient of the calorimetric-cell, W/deg and A_t is the peak area, sec.deg, corresponding to the heat effect. The coefficient K dependence on the temperature T, c was approximated by the formula

$$K = a + bT + cT^2 \tag{2}$$

The instrument was calibrated using metals with known temperatures and heats of fusion (In, Sn, Pb, Zn, Al). For the crucible described above and air as the gaseous medium in the oven $a = 2.55$, $b = 1.2 \times 10^{-2}$, $c = 2.57 \times 10^{-5}$. The standard error of measurement in the interval 20–700 °C using formulas (1) and (2) was estimated to be 5–10%.

3. Results and discussion

In Fig. 1 are presented the DSC curves of some model hydrocarbons used for calibration of the method.

In Fig. 1 the reference material temperature $T2$ is plotted on the X-axis and the differential temperature $T1$–$T2$ on the Y-axis. The temperatures of transitions are indicated as intervals $T2_{\text{in}}$–$T2_{\text{i.p.}}$, where $T2_{\text{in}}$ is the temperature $T2$ where the DSC curve begins to deviate sharply from the baseline and $T2_{\text{i.p.}}$ is the temperature $T2$ where the DSC peak has an inflection point on its descending branch (some distance to the right of the peak summit). It is assumed that at $T2_{\text{i.p.}}$ the reaction is largely over [10].

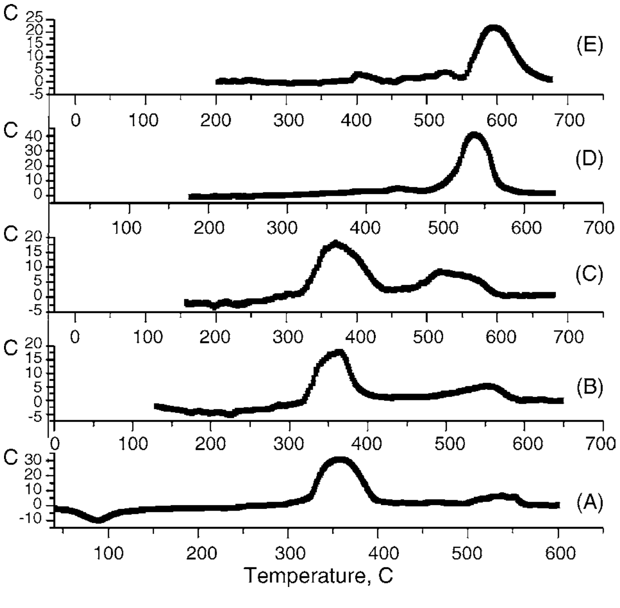

Fig. 1. DSC curves of various petroleum hydrocarbons: A, ceresin; B, medium base lubricating oil; C, heavy base lubricating oil; D, resin extracted from crude oil; E, asphaltene extracted from cude oil.

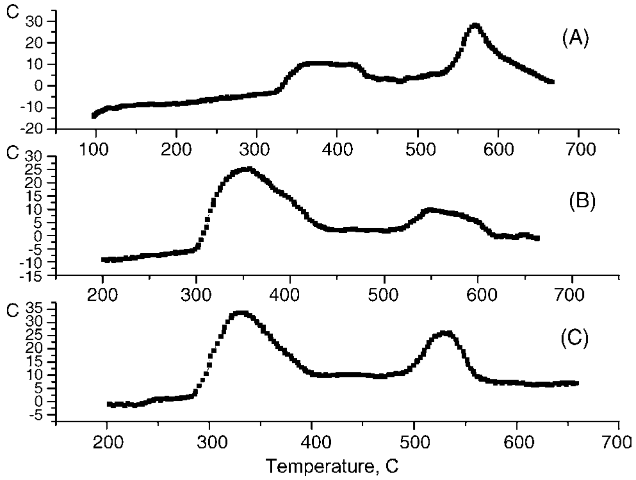

Fig. 2. DSC curves of crude oils of different geological age differing in the content and nature of hydrocarbon constituents. A, young Mordovian crude; B, old Vietnamese crude; C, a still older Kalmik crude.

Ceresin exhibits an endothermic effect at ca. 80 °C and exothermic effects at 330–380 and 500–550 °C. The first of these corresponds to ceresin melting, the second to oxidative distillation of paraffins and oil admixtures and the third to oxidative destruction of resin admixtures (Fig. 1A). Medium base oil undergoes oxidative distillation in the region 320–380 °C and oxidative destruction of resin admixtures at 500–560 °C (Fig. 1B). The heavy base oil has a broader oxidation interval 325–420 °C due to a broader fractional composition and a more pronounced exothermic effect of resin oxidation at 500–580 °C due to a greater resin content than the medium base oil (Fig. 1C). The resin and asphaltene extracted from crude oil oxidize at 500–600 and 550–620 °C, respectively (Fig. 1D and E).

It follows from Fig. 1 that the main constituents of a hydrocarbon mixture, viz. paraffins, naphthenoparaffins (base oils), resins and asphaltenes occupy definite and well separated regions on the temperature scale and can thus be identified and measured independently of each other (see also [7]). Further, these temperature regions have different breadths, proportional to the breadth of distribution of fractions within each constituent. Compare, for example, curves B and C of medium and heavy base oils. Temperatures of oxidation increase as the molecular mass and the boiling point of the constituent increase. In this respect oxidation curves follow the same rules as ordinary distillation ones.

In Fig. 1 were given examples of more or less individual hydrocarbons or their narrow fractions. Fig. 2 presents examples of oxidation of their natural mixtures, viz. three crude oils differing in geological age [13] and thus HC composition. The Mordovian crude is a young heavy oil; the Kalmik is an old light one. The Vietnamese crude occupies a middle position. Their specific gravities are $d_4^{20} = 0.9082,\ 0.8920$ and $0.7300\ \mathrm{g/cm^3}$, respectively. Let us see if the present method can distinguish between crudes of different geological age and in what way.

Fig. 2 demonstrates that indeed the main components of a hydrocarbon mixture oxidize at their expected characteristic temperatures in mainly two regions. From comparison of Figs. 1 and 2 one may conclude than the first region (peak) 300–440 °C belongs to paraffins and oils and the second one 500–620 °C (700 °C) to resins and asphaltenes. The initial part of the first region 300–330 °C belongs mainly to paraffins, the remaining part of it—to base oils. One can note the following regularities of the sample's thermal behavior on passing from younger to older crudes.

1. The first oxidation peak is shifted to lower temperatures and becomes narrower. Its left shoulder increases in height and steepness while its right shoulder goes down. The $T2_{\mathrm{in}}$ temperature (the flare up temperature of paraffins) drops from 320 to 300 °C.
2. Likewise, the resin–asphaltene peak shifts to lower temperatures and becomes narrower, lower and smaller as its right shoulder dwindles down.

The first regularity can be explained if one assumes that old (lighter) crudes contain greater amounts of normal paraffins with $T_{\mathrm{fl}} = 300\ °\mathrm{C}$ and lesser amounts of medium and heavy base oils than the young heavy crudes which, conversely, contain greater amounts of heavy base oils and mainly isoparaffins of ceresin type with $T_{\mathrm{fl}} = 320\ °\mathrm{C}$. The second regularity reflects the structural change of asphaltenes which become less thermally stable as they disintegrate to low-molecular species (resins) in lighter crudes.

In general, the more normal and isoparaffins are contained in a sample, the steeper and higher should be the ascending branch of the paraffinonaphthenic peak, reflecting the high-heat and kinetics of oxidation characteristic of such paraffins.

One can see from Fig. 2 that the Mordovian crude is low on paraffins as the left shoulder of the peak is low and slow. The well developed right shoulder of the peak extending to high-temperatures indicates the presence of high-boiling base oil fractions. Besides, this crude is rich in asphaltene and resin as its resin–asphaltene peak with a big right shoulder, large area and height clearly shows.

The Vietnamese crude is rich in normal paraffins as is evidenced by its low-flare up temperature (305 °C) and sharply increased steepness and height of the ascending branch of the peak. The peak's reduced and narrowed right shoulder points to the reduced content of medium and heavy oils in this crude as compared to the Mordovian one.

The still older Kalmik crude has normal paraffins with the highest oxidation heat as the steep and high-left shoulder of the peak shows. Its flare up temperature has shifted to 300 °C indicating the presence of paraffins of C_{24} type. The right shoulder of the peak is narrower than that of the Vietnamese crude oil, indicating a greater degree of conversion of heavy oils to light ones and these to paraffins. It has the lowest asphaltene content as its resin–asphaltene peak is completely shifted to temperatures 500–600 °C where resins predominantly oxidize.

Above was given a qualitative description of the main features of the thermal behavior of some petroleum hydrocarbons. Below is presented a more elaborate quantitative treatment of the obtained data, aimed at determining percent contents of the main constituents in petroleum products.

To achieve this goal two major tasks should first be solved.

It is evident from curves in Fig. 2 that paraffins, light, medium and heavy base oils oxidize and evaporate consecutively in a rather broad interval 100–150 °C giving rise to a broad exothermic peak of irregular shape. To find the contents of these HC fractions one needs to divide the overall peak into portions corresponding to each fraction, which means that definite assignments should be given to each fraction on the temperature scale of oxidation. So the first task is to find ways and means of deconvoluting the overall peak into constituent sub-peaks.

The second task is to determine oxidation heats of individual hydrocarbons or their narrow fractions, i.e. perform the calibration of the instrument (method).

Calorimetry allows establishing the content of a thermally active ingredient in a mixture by using its overall reaction heat ΔH_n, recorded by the instrument and its reaction heat ΔH_o, determined by the operator beforehand using standard specimens. If ΔH_o of a specimen is not known from the literature, it is found experimentally using formulas:

$$-\Delta H_s = K(T)A_s \tag{3}$$

$$\Delta H_s = \Delta H_o M_s \tag{4}$$

$$\Delta H_o = \frac{\Delta H_s}{M_s} \tag{5}$$

where M_s is the standard specimen's mass, $K(T)$ the coefficient of heat transfer of the calorimetric-cell at temperature T, and A_s is the area of the peak on the heating curve corresponding to the standard specimen's heat effect.

The heat of oxidation ΔH_n of a constituent is calculated from the partial area A_n of the overall peak via formula:

$$-\Delta H_n = K(T)(A_n + \tau(\Delta T2 - \Delta T1)) \tag{6}$$

where $\tau = C/K$ is the time constant of the cell and $\Delta T1$ and $\Delta T2$ (°C), are the left and the right heights of the partial peak.

The weight fraction m% of an ingredient with known ΔH_o can now be found:

$$m\% = \frac{\left(\frac{\Delta H_n}{\Delta H_o}\right) 100}{M} \tag{7}$$

where M is the initial mass of the sample.

Heats of oxidation of hydrocarbons of the type presented in Fig. 1 were determined using sample masses 6–8 mg and a heating rate of 50 °C/min. The results are summed up in Table 1.

In the second column temperatures of beginning of the major oxidation peak T_{fl} (flare up temperature) and of the end of reaction ($T_{i.p.}$) are indicated. In the third column sample mass loss at $T = T_{fl} - 5$ (7 °C) (distillate fraction) is given. The last column lists the oxidation heats of hydrocarbons studied.

In the table average values of oxidation heats are given for 3–4 parallel measurements if one definite compound is studied. The relative standard deviation as a rule does not exceed 10%. If samples of one class from various sources are studied, typical intervals of the values' variation are given.

To obtain the distillate fraction cited in the table, the standard specimen of mass M, heated at the adopted rate of 50 °C/min, was quickly removed from the furnace at a temperature 5–7 °C below T_{fl} and weighed. Then the specimen mass loss (M was found and the distillate fraction α calculated as:

$$\alpha = \left(\frac{\Delta M}{M}\right) 100\%$$

Heats of oxidation were calculated for the sample mass remaining in the crucible using formula:

$$\Delta H_o = \frac{K(T)A_s}{(M - \Delta M)}$$

where A_s is the area of the peak on the heating curve of the standard specimen.

As data in Table 1 show, temperatures and heats of oxidation of normal paraffins increase with their molecular mass and reach a maximum for ceresin, which is composed primarily of long-chain normal and isoparaffins, having, evidently, the highest oxidation heats. Heavy naphthenoparaffins (base oils) have much lower oxidation heats than long-chain normal and isoparaffins. There is a notable difference in oxidation heats between heavy distillate oils (2400 J/g) and heavy residual oils (1800 J/g). The reason for this may be that the former contain more paraffins (are more paraffinic) than the latter.

Division of the overall oxidation peak into constituent sub-peaks and calculation of percent contents of HC fractions is

Table 1
Temperatures and heats of oxidation of hydrocarbons used for calibration of the instrument

Sample	Temperatures of oxidation T_{fl}–$T_{i.p.}$ (°C)	Mass loss of sample at $T = T_{fl} - 5$ (7 °C) (mass%) (distillate fraction)	Heat of oxidation (H_o (J/g)
n-paraffin C_{19}	275–290	44	684
n-paraffin C_{21}	276–302	26	1400
n-paraffin C_{24}	290–324	16	1900
Ceresin	320–380	7	6000–8000
Light base oil I-20A	305–343	16	900
Medium base oil I-40A	315–380	16	1850
Heavy base oil I-50A	320–420	16	2200
Distillate oil 420–500 °C	310–410	10	2400
Distillate oil >500 °C	325–420	12	2600–3200
Residual oil	324–420	12	1800
Resin	500–560		6000–10000
Asphaltene	540–620		15000–40000

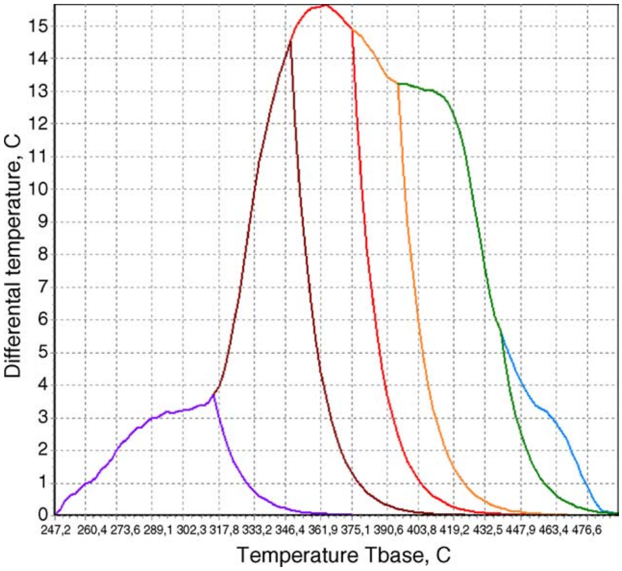

Fig. 3. Naphthenoparaffinic oxidation peak of Mordovian crude oil divided into six sub-peaks by six exponential curves in Deconvolution module.

performed in a special data processing module “Deconvolution” of the program “Thermo” supplied with the instrument “Thermodat”. Its mode of operation is described below using as examples the thermograms of crude oils of Fig. 2.

The operator draws a baseline under the peak to be studied and accesses the module. A detailed and enlarged graph of the peak appears on the screen (Fig. 3).

In the Deconvolution module the regularities of the thermal behavior of crude oils discussed earlier in connection with Fig. 2 are seen much better and in greater detail, allowing more or less accurate peak deconvolution.

In the module DTA peaks are presented as the additional temperature of reaction $\Delta T_r = T1 - T_{base}$ plotted against T_{base} [8].

In this module the overall peak can be divided into as many sub-peaks as there are fractions in the sample. To do this the operator places the pointer of the mouse on the curve at a point where, presumably, one reaction ends and another starts, presses the left button and an exponential curve is dropped from the point chosen onto the baseline. The last curve must be drawn from some point on the final exponential tail branch of the overall peak.

The exponent mimics the tail branch of the peak corresponding to one reaction (substance) [10]. Its shape (curvature) can be changed by putting an appropriate value of the cell’s time constant τ into the check box on the operator panel. We use $\tau = 10$ s for the first major peak 300–450 °C and $\tau = 6$ s for the second peak 500–700 °C as approximate average values.

Let us introduce some terms and define some rules for describing and analyzing oxidation peaks of hydrocarbon mixtures.

The overall peak (peak for short) in Fig. 3 can be considered to consist of several closely situated sub-peaks overlapping one another. The first one from 240 to 320 °C can be termed the left wing, or the left satellite of the main peak. It ends at a characteristic point of the curve corresponding to the flare up temperature T_{fl} of the hydrocarbon mixture.

The main peak starts from T_{fl} and ends at 400 °C (440 °C) where another characteristic point is situated separating it from the right wing, or the right satellite of the main peak. The latter may consist of several, usually four sub-peaks; the rules for their finding are given below. Let us first consider the notion of the characteristic point of the curve.

The characteristic point (ChP for short) of the curve is by definition the point where the curve has a maximum downward curvature (the inflection point) and from which the exponent is dropped onto the baseline. It is assumed to correspond to the temperature where one reaction ends and another starts. Between two ChP’s the point of a maximum upward curvature is situated—the summit of a sub-peak. This is the center of a particular fraction distribution. Drawing exponents from two ChP’s flanking the summit is equivalent to separating the fraction from its neighbors.

As often as not the summits are poorly defined and the position of the ChP’s on the curve must be guessed at. Still, a successful deconvolution can be performed in the majority of cases.

The first step in deconvoluting the main peak is to find the summits and then the ChP’s flanking them on its ascending and descending branches. In the case of the Mordovian crude the ChP’s seem to be the following: 320 (T_{fl}), 354, 380, 400, 440 °C. Thus, five sub-peaks can be generated by the known procedure using these ChP’s.

The following interpretation of the peak in Fig. 3 can now be given.

The left satellite of the peak most likely corresponds to the oxidation of heavy paraffins in the distillate fraction that in young crudes have not had time to disintegrate to low-molecular species.

The first sub-peak of the main peak may correspond to the oxidation of paraffins. The second, third and fourth sub-peaks should then correspond to the oxidation of light, medium and heavy oil fractions.

The small right wing of the peak from 440 to 480 °C may corresponds to the oxidation of light resins that are present in young oils and absent in old ones. Its small size may be due to their small content or their low-oxidation heat.

Taking the temperatures of the characteristic points of the curve as borderlines between separate HC fractions, one can give the following assignment of oxidation intervals to isoparaffins, light, medium and heavy base oils of a heavy crude oil (Table 2).

The temperatures of characteristic points may vary by about 5 °C for different heavy crude oils; therefore, in the table they are given with a possible interval of their variation.

Now that the first task (that of peak deconvolution) has been solved and oxidation heats of the main HC components are known (Table 1), one can proceed to the percent contents determination of HC fractions.

In studying oils, as all other HC volatile products, it is necessary to know the fraction evaporated from the crucible by the time the major exothermic effect starts. Calorimetry cannot provide this information, as one does not know what part of the

Table 2
Temperatures of oxidation of isoparaffins, light, medium and heavy base oils in heavy crude oils with flare up temperatures 325 ± 5 °C

	Distillate heavy paraffins	Solid paraffins	Light oil	Medium oil	Heavy oil
Oxidation intervals, $T1$–$T2$ (°C)	240 − 320 ± 5	320–350 ± 5	350–385 ± 5	385–400	400–440

distillate evaporates with and what part without the heat effect. Therefore, some other method should be used. In the case discussed, the sample, while being heated from room temperature at the rate of 50 °C/min, is rapidly removed from the furnace at temperature some 5–7 °C below the flare up point T_{fl} and the weight fraction lost (distillate α%) determined gravimetrically.

A fresh sample of the same material is heated to 440 °C, then removed from the furnace and weighed. The weight fraction γ of resin + asphaltene remaining in the crucible is found and the fraction β = paraffins + base oils is calculated via formula:

$$\beta = 100\% - (\alpha + \gamma)\% \qquad (8)$$

The method delineated above gave for the Mordovian crude $\alpha = 44$, $\gamma = 14$ and $\beta = 42\%$.

After peak deconvolution the program determines the partial peak areas A_{n} and calculates ΔH_{n} for each sub-peak (fraction) and its percent contents via formulas (6) and (7). Before that the operator must input the values of the initial sample mass M into an appropriate checkbox on the operator panel and the fraction's oxidation heat ΔH_{on} into a special table of the module. The choice of ΔH_{on} values is governed by three rules. The first one demand that the content of the β fraction found calorimetrically is more or less equal to the β value obtained gravimetrically. The second rule recommends choosing for the lighter oil fractions somewhat greater values of ΔH_{o} than for the heavier ones, assuming that the lighter fractions of base oils contain greater amounts of high-energy paraffins. Tentatively one may use ΔH_{on} values decreasing by 5–10% at each consecutive step. The third rule recommends choosing for the paraffinic fraction of young heavy crudes oxidation heats on the order of 6000 J/g and for old light ones those on the order of 7000 J/g.

Following these rules, the values of $\Delta H_{\mathrm{o}} = 6000$, 3000, 2600 and 2400 J/g were chosen to give 5.0, 16.0, 10.3 and 10.9 for the solid paraffins, light, medium and heavy oils, respectively. Their sum equals 41.2%, which is close to the gravimetric value 42.0%.

The value for the distillate paraffins—19.5% if $\Delta H_{\mathrm{o}} = 500$ J/g is a rough approximation good only for comparison purposes as no exact ΔH_{o} value for them can be found based on gravimetric calibration.

Let us now consider the case of the lighter Vietnamese and Kalmik crude oils. Their deconvoluted peaks are shown on Fig. 4 and the weight loss method has given $\alpha = 37\%$ (distillate), $\gamma = 6\%$ (resins), $\beta = 57\%$ (paraffinonaphthenes) for the first crude and $\alpha = 56$, $\gamma = 6$ and $\beta = 38\%$ for the second.

Applying to the peaks of Figs. 4 and 5 deconvolution rules formulated earlier, results given in Table 3 were obtained.

In Table 3 columns 2–7 contain temperature intervals assigned to each HC fraction, as well as their heats of oxidation and percent contents. Column eight gives distillate and asphaltene/resin contents determined gravimetrically as the sum $\alpha + \gamma$ and beneath them the value of $\beta = 100 - (\alpha + \gamma)\%$. The calorimetric-value of β is also given.

Comparing data for the three crude oils in the table the following regularities can be noted on passing from younger (heavier) to older (lighter) crudes.

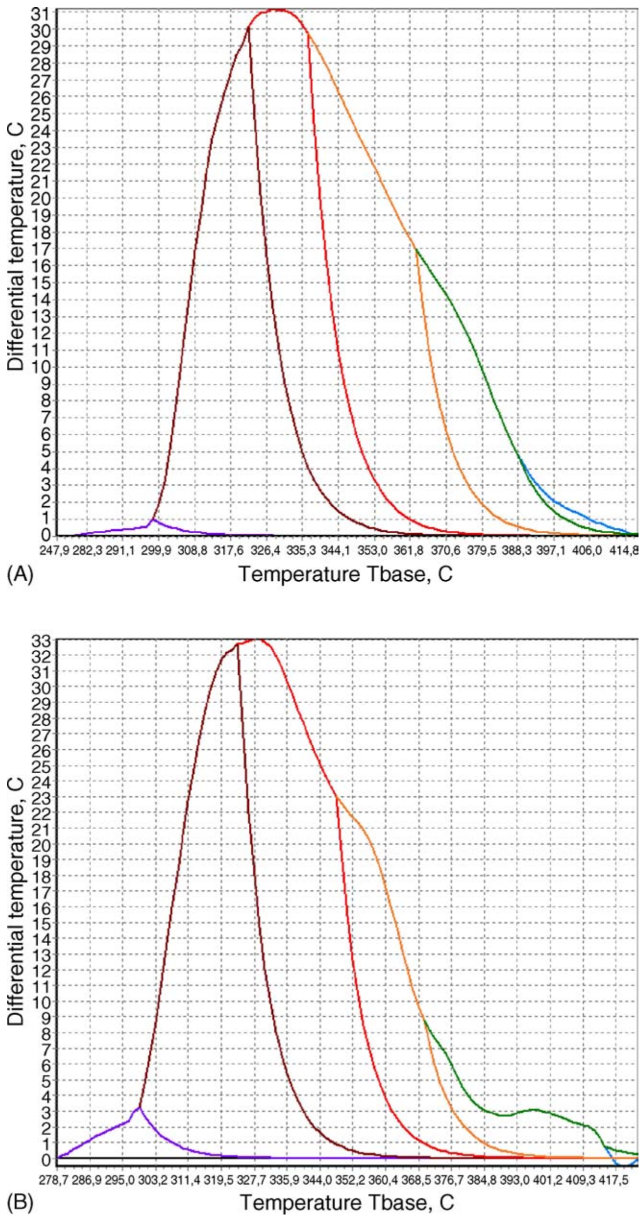

Fig. 4. Oxidation peaks of Vietnamese and Kalmik crude oils. (A) Paraffinonaphthenic oxidation peak of Vietnamese crude oil. (B) Paraffinonaphthenic oxidation peak of Kalmik crude oil.

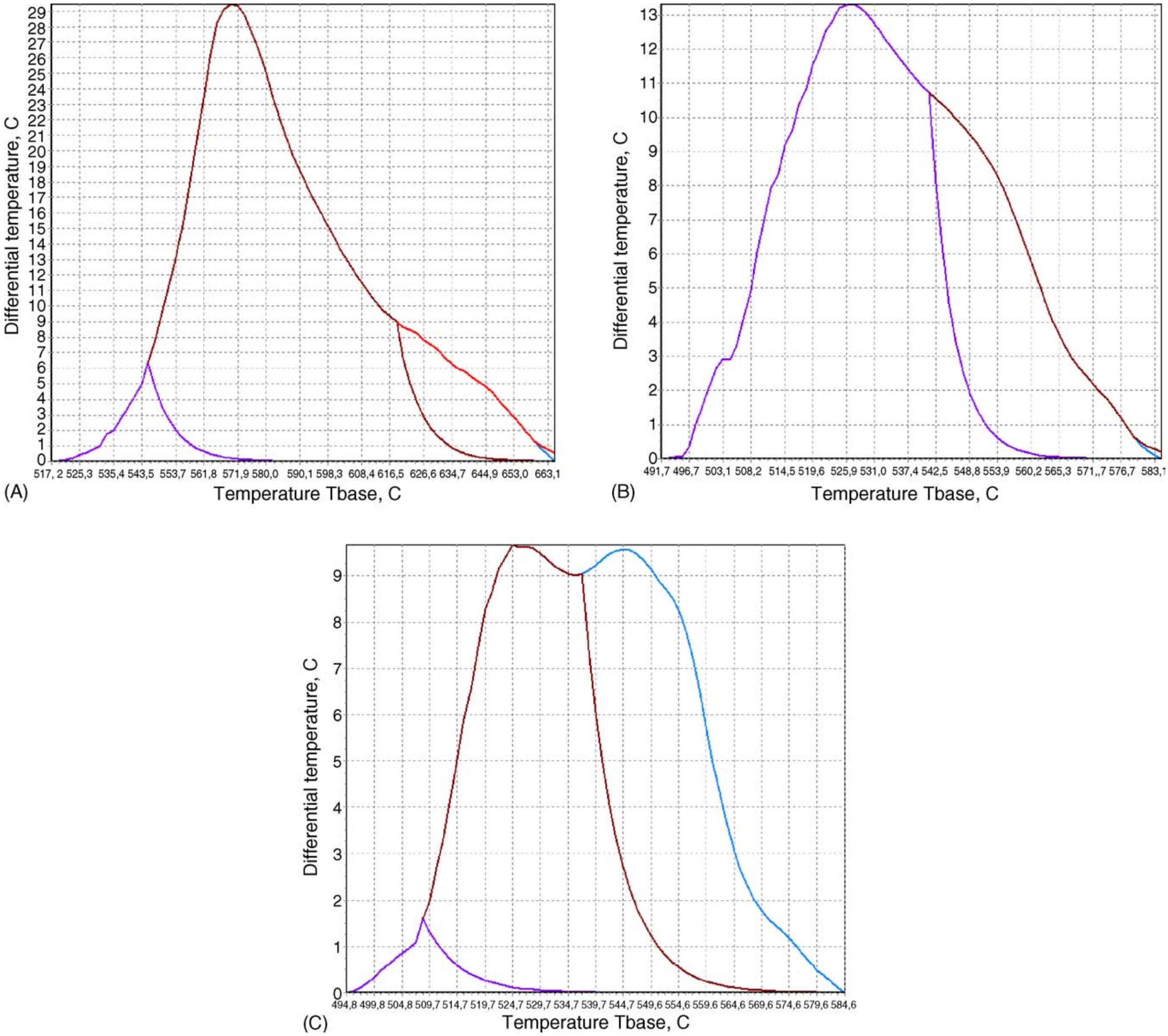

Fig. 5. Resin/asphaltene oxidation peaks of young Mordovian and old Vietnamese and Kalmik crude oils. (A) Resin/asphaltene oxidation peak of Mordovian crude oil. (B) Resin/asphaltene oxidation peak of Vietnamese crude oil. (C) Resin/asphaltene oxidation peak of Kalmik crude oil.

1. Oxidation intervals of all the four HC fractions are shifted to lower temperatures.
2. Oxidation heats of all the HC fractions become progressively higher.
3. Old light crudes do not practically contain heavy paraffins in their distillate fractions.

Regularity 1 can be explained if we assume that as the crude ages its paraffins and oils disintegrate to give fractions of lower molecular weight and of lower boiling point.

Regularity 2 can be explained on the assumption that paraffins have much greater oxidation heats than base oils, so the greater their content in the sample, the greater is its heat of oxidation. As the crude ages, more and more oils disintegrate to give more and more long-chain normal and isoparaffins with great oxidation heats. This is a rather important finding as it points to the possibility of formulating an objective criterion for estimating paraffinic and base oil potentials of a given crude oil (see below).

Regularity 3 can be explained on the assumption that distillate heavy paraffins in old crude oils have had sufficient time to disintegrate to low-molecular compounds evaporating in the interval 200–300 °C without oxidative cracking.

Data of Table 3 can also be used to mark out three general classes of crude oils.

The first class comprises young heavy crudes with the following distinctive features: (i) small distillate fraction (35–42%); (ii) large asphaltene/carbine content (12–15%); (iii) high-proportion of heavy high-boiling oils; (iv) low-oxidation heats pointing to a low-content of high-energy paraffins in the oil fractions. This is the case for the Mordovian crude which may be considered to be its typical member, its thermogram serving as a thermal passport (fingerprint) of this class of crudes.

Table 3
Temperatures and heats of oxidation of HC fractions of heavy, medium and light crude oils

	Distillate heavy paraffins	Solid paraffins	Light oil	Medium Oil	Heavy Oil	Resin	Asphal-tene	Distillate + A/R gravimetrically $(\alpha+\gamma)\beta$
Mordovian heavy crude oil								
Oxidation intervals								
$T1$–$T2$ (°C)	240–320	320–346	346–380	380–403	403–440	530–542	542–616	44 + 14
$T2$–$T1 = \Delta T$ (°C)	80	26	34	23	37	12	74	42
Oxidation heat (J/g)	500	6000	3000	2600	2400	14000	16000	
Fraction content (mass%)	19.5	4.96	16.0	10.3	10.9	1.0	12.1	42.2
Vietnamese medium crude oil								
Oxidation intervals								
$T1$–$T2$ (°C)	252–296	296–342	342–368	368–389	389–440	500–538	538–614	37 + 6
$T2$–$T1 = \Delta T$ (°C)		46	26	21	51	38	76	57
Oxidation heat (J/g)	500	4600	4300	4200	4000	14000	17000	
Fraction content (mass%)	2.8	22.8	14.4	8.6	10.9	2.46	3.8	56.7
Kalmik light crude oil								
Oxidation intervals								
$T1$–$T2$ (°C)		302–333	333–356	356–377	377–437	497–537	537–575	56 + 6
$T2$–$T1 = \Delta T$ (°C)		31	23	21	60	40	38	38
Oxidation heat (J/g)		6800	6600	6400	6200	16000	18000	
Fraction content (mass%)		16.1	11.5	4.1	5.9	3.74	2.2	37.6

On the other extreme is the class of old light crudes having the following distinctive features: (i) large distillate fraction (50–60%); (ii) low-resin/asphaltene content (about 6%); (iii) low-proportion of high-boiling oils; (iv) large oxidation heats pointing to the presence of high-energy (normal) paraffins. This is the case for the Kalmik crude—a typical representative of this class of crudes. Its thermogram may serve as a thermal passport (fingerprint) of the class of old light crudes.

A great variety of crude oils fill the second class intermediate between the above two and sharing in different proportions their typical features. The Vietnamese crude evidently belongs in this class as it has distinctive features of the both extreme cases, viz.: a large paraffinic content (22.8%), high-oxidation heats (4600 J/g) and a small asphaltene content (6%) place it evidently in the third class of light crude oils; a large content of heavy oils (10.9%); a small distillate fraction (37%) place it in the first class of heavy crude oils. It may be said that the crude has retarded cycles of transformation of heavy oils to middle and light ones and of long-chain paraffins to low-molecular distillate species. This explains the accumulation of oils in the crude and the reduced content of the distillate fraction.

Regularity 2 noted above can be put to good use in the following way. Let us assume that naphthenoparaffins forming the bulk of heavy crude oils practically devoid of paraffins have the lowest oxidation heat ΔH_{oil} of say 1800 J/g—a value close to oxidation heats of some base oils, see Table 1. Let us further assume that the maximum oxidation heat ΔH_{par} of a purely paraffinic fraction equals say 8000 J/g—a typical oxidation heat of ceresin (Table 1). Let us denote the relative paraffinic fraction in the crude by X and the relative oil fraction by Y. Then we can write the following equations for the oxidation heat ΔH_{exp} found experimentally:

$$\Delta H_{\text{exp}} = \Delta H_{\text{par}} X + \Delta H_{\text{oil}} Y \qquad (9)$$

$$X + Y = 1 \qquad (10)$$

Solving this system of two equations with two unknowns X and Y we get:

$$X = \frac{(\Delta H_{\text{exp}} - \Delta H_{\text{oil}})}{(\Delta H_{\text{par}} - \Delta H_{\text{oil}})} \qquad (11)$$

$$Y = 1 - X \qquad (12)$$

which are the formulas for calculating the unknowns X and Y; the latter may be termed paraffinic and base oil potentials, respectively, of a crude oil.

Let us apply Eqs. (11) and (12) to the three crude oils of Table 3.

From Table 3 the average oxidation heats ΔH_{exp} of the heavy, medium and light crude oils are 3500, 4400 and 6500, respectively (all the four fractions are summed up). Thus for the Mordovian crude we have:

$$X = \frac{(3500 - 1800)}{(8000 - 1800)} = \frac{(35 - 18)}{(80 - 18)} = \frac{17}{62} = 0.27$$

$$Y = 1 - 0.27 = 0.73$$

For the Vietnamese crude we get:

$$X = \frac{(44 - 18)}{62} = 0.42$$

$$Y = 1 - 0.42 = 0.58$$

and for the Kalmik crude:

$$X = \frac{(65 - 18)}{62} = 0.76$$

$$Y = 1 - 0.76 = 0.24$$

Table 4
Percent contents of the light and heavy resins, asphaltene and carbine in Mordovian, Vietnamese and Kalmik crude oils

	Light resin	Heavy resin	Asphal-tene	Carbine
Oxidation intervals				
$T1$–$T2$ (°C)		520–545	545–620	620–660
$T2$–$T1$ = ΔT (°C)		25	75	40
Oxidation heats (J/g)		14000	16000	18000
Fraction content (mass%)		1.02	12.11	1.2
Oxidation intervals				
$T1$–$T2$ (°C)		495–543	543–583	
$T2$–$T1$ = ΔT (°C)		48	40	
Oxidation heats (J/g)		14000	17000	
Fraction content (mass%)		2.46	3.82	
Oxidation intervals				
$T1$–$T2$ (°C)	494–510	510–537	537–575	
$T2$–$T1$ = ΔT (°C)	16	27	38	
Oxidation heats (J/g)	12000	16000	17000	
Fraction content (mass%)	0.32	3.42	2.17	

As was to be expected, the base oil potential of the heavy crude is the greatest—0.73 or 73% and the paraffinic potential the lowest—0.27 or 27%. The Kalmik oil has the highest paraffinic potential 76% and the lowest oil one—24%. The Vietnamese crude is somewhere in the middle, its oil potential being 58%.

Finally, let us see what useful information can be extracted from the oxidation peaks of the resin/asphaltene fraction of the three crude oils of Table 3. Their respective deconvoluted peaks are shown on Fig. 5 and the results of calculations are summed up in Table 4.

Resin/asphaltene oxidation peaks were deconvoluted according to rules given earlier. Exponents were drawn from inflection points as shown in Fig. 5, as a result 2 or 3 sub-peaks were obtained, marking out oxidation intervals of the main resin/asphaltene fractions. In the case of the Mordovian crude these proved to be 530–542, 542–616 and 616–653 °C; the intervals may be assigned to heavy resin, asphaltene and carbine, respectively. Fig. 5A and data of Table 4 show that this crude contains some undegraded carbine (1.2%), asphaltene (12.11%) and some heavy resin (1.02%). These values were obtained using the oxidation heats indicated in the table.

The results show at what stage of decomposition each component of the resin–asphaltene–carbine mixture finds itself. The carbine component has, evidently, decomposed almost entirely, as only 1.2% of a lower molecular weight carbine fraction is left of it. The asphaltene fraction has just begun decomposing giving 1.02% of heavy resin. Relative percents of the fractions, starting with hard resin, are: 7.0, 84.5 and 8.5% (rel.). These figures show the distribution of the corresponding fractions in the HC mixture.

On passing to older crudes oxidation intervals of all fractions shift progressively to lower temperatures as the fraction amounts decrease rapidly, the center of their distribution moving to heavy resins. In the Vietnamese crude the amount of asphaltene has gone down to 3.8% and the resin content has increased to 2.46%, which shows that the resin has further transformed to lower weight molecular species. This process of consecutive degradation is also seen in the Kalmik crude, in which some light resin appears for the first time. All this shows that the high-molecular weight HC compounds of the oil mother-matter (kerogen) can indeed transform to lower molecular weight species, analogous to the naphthenoparaffins and there is a direct proportionality between the degrees of degradation of these two major constituents of a crude oil.

Data in Table 4 can be used for establishing the coke-forming potential of a crude oil. The rule for calculating this potential can be derived on the assumption that only asphaltenes and carbines favor the coke-formation, thus their absolute (mass) and relative percent contents may serve as a quantitative index of the coke-forming potential. Then grouping together the percent contents belonging to the asphaltene/carbine fraction, we get an approximate amount of a high-quality coke that can be obtained from a crude oil. It does not mean that coke cannot be produced from resins, but then it will be, evidently, a coke of an inferior quality.

4. Conclusions

1. The choice of experimental conditions favoring a full (complete) sample oxidation has allowed step by step consecutive oxidation of narrow fractions of a hydrocarbon mixture, beginning with normal and/or isoparaffins and ending with asphaltenes and carbines.
2. The use of a scanning calorimeter of the isolated container type with high-calorimetric-resolution and sensitivity has allowed a reasonably accurate determination of the temperatures and heats of oxidation of the main constituents of crude oils, thus enabling their detailed quantitative and qualitative fractional analysis.
3. In conformity with the theory of organic genesis of crude oils it has been shown that as the oil ages it accumulates normal paraffins and loses high-boiling base oils, resins and asphaltenes (it becomes more paraffinic in all its fractions). Evidently, the DSC curve may serve as an indicator of the genesis and degree of maturation of a crude oil.
4. The results of the present study demonstrate the great and as yet little realized potential of the thermal methods of

analysis. Their possible areas of application, to mention just a few, are: oil geochemical research, e.g. oil aging studies and oil prospecting, ecological monitoring, e.g. oil finger print identifications, establishing new classification schemes for a great many known (studied) and new (unstudied) crude oils and related materials.

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