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Fractional and component analysis of crude oils by the method of dynamic microdistillation—Differential scanning calorimetry coupled with thermogravimetry

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Abstract

High-resolution differential scanning calorimetry was used to accurately establish the temperature intervals of oxidation/distillation of the major components of crude oils. Some theoretical aspects of the method of dynamic microdistillation, enabling consecutive distillation (oxidation) of the main components of hydrocarbon mixtures, are discussed. The experimental TG-DSC curves show that the temperature scan of the run can be divided into six regions, of which the first belongs to simple distillation of the sample's liquid constituent (the distillate) and the others to oxidative cracking distillation of the solid (heavy) residue. The latter occur in the order paraffins + light oils, middle base oils, heavy base oils, condensed aromatics (resins) and asphaltenes. The probable oxidation mechanisms of different classes of petroleum hydrocarbons operating in different temperature regions are discussed. Full quantitative fractional and group component analysis of a number of crude oils of different chemical classes and geological age was carried out by the combined TG-DSC techniques under specially chosen experimental conditions (those of dynamic microdistillation).

Keywords: Crude oils; Fractional composition; Differential scanning calorimetry; Thermogravimetry

1. Introduction

Heating a crude oil under proper experimental conditions results in consecutive distillation of its constituent parts, first of the distillate fractions such as benzine, ligroin, kerosene, gas oil, then of the heavy (solid) residue: paraffins, light, middle and heavy base oils, condensed aromatics (resins) of progressively greater molecular mass and asphaltenes. It was shown earlier [1] that the lighter part of the crude oil undergoes simple distillation, while the heavier part—oxidative cracking distillation (in air atmosphere). The latter proceeds with pronounced exothermic heat effects and can be monitored calorimetrically. Kök [2] found that on combustion in air of two heavy crude oils three different reaction regions can be identified as low temperature oxidation, fuel deposition and high-temperature oxidation. The results of TG/DSC studies on heavy oil cores by Verkocy and Kamal [3] also point to at least three groups of chemical reactions occurring in three temperature regions. Kök et al. [4] performed kinetic analysis of oxidation of the main components of crude oils obtained from them by column adsorption chromatography to establish the intervals at which evaporation, oxidation and combustion operate for each fraction. Levinter and Medvedeeva [5] suggested a reaction scheme including visbreaking and cracking for the oil heavy residue at temperature above 300 °C. In this region, the C–C bonds are broken producing reactive free radicals leading to the formation either of low molecular species (gases) or condensed ones (resins) [6]. Goncalves et al. [7] studied asphaltenes from crude oils by combined TG-DTA/GC/MS techniques. An extensive bibliography on the subject can be found in the literature survey by Kök [8].

The noted properties (consecutive distillation, exothermic heat effects) lend themselves well for developing an analytical method of fractional (component) analysis of crude oils and its derived products. In fact, the weight loss curve of a sample can be used for the purpose, provided the temperature intervals of evaporation/oxidation of different crude oil fractions are accurately known. These can be determined calorimetrically, at least for the crude oil heavy residue. It is an accepted practice to record simultaneously TG and DSC curves to facilitate the interpretation

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of events taking place in the heated sample. Unfortunately, the calorimetric resolution of the existing DSC and DTA instruments is too low (especially at high temperatures) to allow the exact pinpointing of the oxidation intervals of separate hydrocarbon fractions. Besides, the experimental conditions necessary for the obtainment of reliable experimental results are not well known due to insufficient knowledge of the high-temperature properties of petroleum hydrocarbons. The present work addresses these issues from the experimental and theoretical points of view.

The author's differential scanning calorimeter "Thermodat" was used for the present study, in which some important changes from the conventional analogs were implemented to obtain a better resolution of thermal events taking place in the sample at temperatures in the range 300–700 °C [9–11].

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 lowered into a vertical tube furnace open from the lower and upper ends to insure good furnace ventilation (due to natural convection). Samples of 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 air and heating rates of 45–50 °C/min were commonly used. Total heat effects ΔH_t and partial heat effects ΔH_n, J of thermal reactions were calculated using the formula:

$$-\Delta H_\mathrm{t} = K A_\mathrm{t} \tag{1}$$

for the full reaction (total peak area A_t, degree × s), and

$$-\Delta H_\mathrm{n} = K(A_\mathrm{n} + \tau(\Delta T_2 - \Delta T_1))$$

for partial reactions (partial peak areas A_n), for details see [1], where K is the heat transfer coefficient of the calorimetric cell (W/degree), τ the cell time constant, ΔT_1 and ΔT_2 are the left and right heights of the partial peak. 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 relative standard deviation for five to six measurements in the interval 20–700 °C using formulas (1) and (2) was estimated to be 5–10%.

As an example of the method's performance the TG-DSC curves of a Kazakh crude oil (specific gravity $\rho_{15}^{15} = 0.8728$) are given in Fig. 1. In the figure, the reference temperature T_2 is plotted on the X-axis, the weight loss (wt%) on the left ordinate and the DSC peak height, ΔC, on the right ordinate. Evaporation/oxidation intervals are given in the first line above the curves, the components' symbols – in the second, and their wt% contents – in the third line.

The figure shows that by 298 °C, the sample loses 54% of its weight due to the light distillate portion of the crude without noticeable heat effects on the DSC curve. At 298 °C, a sharp exothermic effect on the DSC curve appears signaling the beginning of oxidation of the crude oil heavy residue. The heat

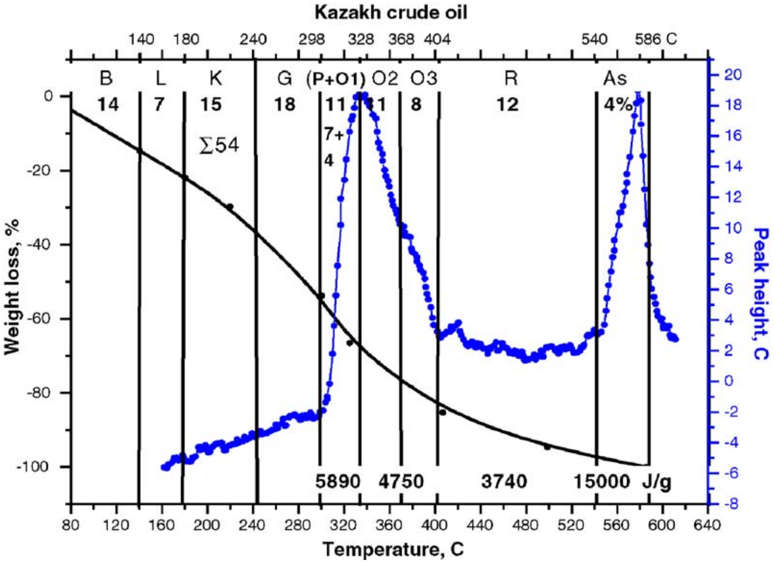

Fig. 1. TG-DSC curves of a Kazakh crude oil of Blinov oil field.

evolution continues with varying degree of intensity till 586 °C when finally all the material in the crucible is volatilized (the crucible is empty after the run).

It follows from the shape of the DSC curve that at least five regions can be singled out in the oxidation interval 300–600 °C, each corresponding to different components of the heavy residue with different mechanisms (heats, kinetics) of oxidation. These will be considered below. A more detailed treatment of the subject is given in [1].

(1) *Region* $T_{\rm fl}$–$T_{\rm 1top}$ from the beginning of the first exothermic peak to its top point, where $T_{\rm fl}$ is the flare up temperature of the solid residue, and $T_{\rm 1top}$ is the T_2 temperature corresponding to the peak top (maximal ΔT of reaction, see the right ordinate). To learn the actual temperature of the sample, ΔT should be added to T_2.

   On the DSC curve, this region corresponds to the ascending branch of the peak (its left shoulder). In this region solid normal paraffins and light base oils undergo oxidative cracking and distillation of oxidized fragments.

   What has been said is fully applicable to highly paraffinic crude oils. For crudes containing little paraffins and much base oils the region of the paraffins is narrowed, their top point is situated on the ascending branch of the peak (is practically not visible), and the first peak summit belongs not to paraffins (as in Fig. 1) but to base oils—the case of the Mordovian crude described in [1].

(2) *Region* $T_{\rm 1top}$–$T_{\rm 1inf}$ from the top point of the peak to the inflection point on its descending branch. Here the middle base oils oxidize and evaporate.

(3) *Region* $T_{\rm 1inf}$–$T_{\rm 1end}$ from the inflection point to the end point of the first peak. Here, the heavy base oils oxidize and evaporate.

(4) *Region* $T_{\rm 1end}$–$T_{\rm 2st}$ extending from the end of the first peak to the start of the second peak, where resins oxidize and evaporate.

(5) *Region* $T_{\rm 2st}$–$T_{\rm 2end}$ of the second exothermic peak where asphaltenes oxidize and leave the crucible as gases.

It is evident from the shape of the DSC curve that the characteristic points $T_{\rm fl}$, $T_{\rm inf}$, etc., can be used to exactly pinpoint the intervals on the TG curve of the components leaving the crucible, and thus determine their contents in the mixture. To do this, perpendicular lines are drawn through the characteristic points on the DSC curve and their points of intersection with the TG curve projected on the left ordinate of the graph, from which the components' contents are read. As regards the region where the light portion of the crude leaves the crucible, it is divided more or less arbitrarily as shown on the graph, and intervals T–140, 140–180, 180–240, 240–$T_{\rm fl}$ (°C) are assigned to benzine, ligroin, kerosene and gas oil fractions of the distillate portion of the crude, respectively.

The TG curve in this study was obtained in the following manner. Two crucibles containing 18–20 mg sample each were heated at the adopted rate to a predetermined temperature, the crucibles' supporting rod raised to the upper end of the furnace and one crucible quickly removed from the thermocouple and weighed. The other crucible was removed in the like manner at a temperature 30–50 °C higher than the first one. Fresh samples were loaded in the crucibles and the experiment repeated at higher temperatures. In this way about 8–10 points were obtained sufficient for building a TG curve in the temperature interval studied.

The described method may be termed "the method of stopped (freezed) reaction" well known in the field of kinetic studies. As applied to the mixture evaporation process, it deserves some explanatory remarks.

Consider a droplet of liquid heated at some constant rate under conditions of free gas exchange (open space with good natural convection). As the temperature of saturation of a volatile constituent at a given (atmospheric) pressure is approached, it begins to leave the droplet at a rate proportional to its volatility. The less volatile fractions of the mixture will begin to leave the droplet at some higher temperatures, and thus their separation will become possible.

The dynamic heating regime is essential for good fraction separation because at high-heating rates the less volatile fraction will not have the time to evaporate at low temperatures but only at those close to the saturation ones. Even if heating rates 40–60 °C/min are used, no overheating is expected due to the absence of diffusion limitations (thin-sample layer, free gas exchange). Though under heating is possible, as at low or zero heating rates all the fractions will have time to evaporate at low temperatures far removed from their saturation ones.

The results presented in Fig. 1 seem to bear out this reasoning, as the distribution of distillate fractions of the crude shown on the figure is rather close to the one obtained by standard means. It should be noted here that to obtain kerosene and gas oil fractions from a crude by conventional methods, costly high-vacuum equipment and great sample masses must be used, so the advantage of the described simple method over the conventional one is quite evident.

Now the mechanisms of the thermal reactions in regions 1–5 will be considered in some detail.

The high kinetics and heat of the reaction reflected in the narrow shape and great height of the first peak on the DSC curve point to the mechanism of the reaction as being that of oxidative cracking characteristic of long-chain (solid) paraffins ($C > 18$). Oxidative cracking involves the fission of the molecule's C–C bond through peroxides formation and decomposition resulting in the free radical formation and chain propagation. This kind of reaction is known as detonation observed in low octane number fuels containing normal paraffins with $C > 6$. The fission of the C–C bond occurs in the middle of the chain where the bond's energy is the lowest, so oxidized paraffin chains of lower molecular mass are formed and instantly vaporized being overheated at the temperature of their formation. This can be seen as heavy whitish fumes beginning rapidly to leave the furnace on the appearance of the first peak on the DSC curve. The fumes have a slight paraffinic odor which changes to an unpleasant odor of engine exhaust gases (oxidized oils) at temperatures of the descending branch of the peak.

The temperatures of the components oxidative distillation are governed not by the C–C bond activation energy but by activation energies of vaporization, and are thus proportional to molecular masses and boiling points of the components. This can be explained by the fact that before the C–C bond fission the molecule must acquire the free volume necessary for large-amplitude vibrations leading to the C–C bond breaking. Thus, the intermolecular interactions must first be overcome, and this is equivalent to microscale evaporation with the consequences mentioned above.

It was shown in [1] that oxidation heats of solid paraffins of the ceresin type are on average 8000 J/g and those of base oils 1800 J/g. The temperatures of oxidation T_{fl} of normal paraffins and light base oils lie in the interval 280–315 °C, and those of the middle and heavy base oils in the interval 320–330 °C. So we have all the grounds to ascribe the ascending branch of the first peak on the DSC curve to normal paraffins and light oils, and the descending branch to middle and heavy base oils, respectively, see Fig. 1.

The great difference in the oxidation heats of paraffins and base oils can be used for their separate determination in the interval T_{fl}–T_{top}. Assuming that the overall experimental heat of oxidation in this interval is the additive sum of oxidation heats of paraffins and base oils, two equations with two unknowns can be written down:

$$\Delta H_{\mathrm{exp}} = \Delta H_{\mathrm{par}} X + \Delta H_{\mathrm{oil}} Y$$

$$X + Y = 1$$

where X and Y are the fractions of paraffins and base oils, respectively, ΔH_{par} and ΔH_{oil} are their oxidation heats and ΔH_{exp} is the experimental heat (J/g).

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

$$X = \frac{\Delta H_{\mathrm{exp}} - \Delta H_{\mathrm{oil}}}{\Delta H_{\mathrm{par}} - \Delta H_{\mathrm{oil}}} \tag{3}$$

$$Y = 1 - X \tag{4}$$

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.

Formulas (3) and (4) are used to calculate the contents of paraffins and base oils of crude oils whose TG-DSC curves are presented in Fig. 2.

It can be deduced from the general shape (oxidation profile) of the DSC curve that the oxidation heat is high for the paraffin + light oil component, then it falls abruptly in the region of resin oxidation 400–500 °C, after which it sharply increases in the region of asphaltene oxidation 500–600 °C. It is evident that different oxidation mechanisms characteristic of different classes of hydrocarbons operate in these regions.

Low temperature oxidation of hydrocarbons at 300–400 °C is a low intensity one leading to the formation of large-oxidized fragments, and thus low heats (proportional to the number of oxidized species). It is not plasma oxidation (not burning), as no light emission or flames accompany this process. High heats observed nevertheless in this region are evidently the result of peroxide formation and decomposition.

Middle temperature oxidation of resins in the region 400–500 °C produces little heat, and this results in the flat low portion on the DSC curve separating the first and second peaks on the DSC curve. This low heat can be explained by a very high viscosity of the resin melt into which the oxygen cannot readily penetrate. Large bubbles are formed in the viscous mass by the gases of pyrolysis so that the sample rises over the crucible as a large-porous mass. Evidently, large-positive heats are required to overcome the resin intermolecular interactions further reducing the resultant negative oxidation heats.

High-temperature oxidation of asphaltenes and carbines in the region 500–600 °C (700 °C) proceeds with an exceptionally high heat. This is due to the change of oxidation mechanism, which is now not that of oxidative cracking but that resembling plasma oxidation (burning). When strong intermolecular interactions of the long-chain closely packed asphaltene molecules are overcome, the molecules find themselves at temperatures (500 °C and higher) where the activation energies of fission of the most stable C–C, C–H and other bonds are reached, and thus a great number of small molecules of the type CO, CO_2, H_2O are formed with the resultant high-oxidation heats. Light is emitted by the sample—the sample glows red and occasionally flames appear as white spots amid the glowing mass. These produce the greatest heat giving rise to increased upward slopes on the second oxidation peak on the DSC curve.

Experiment shows that every chemical class of crude oils has a characteristic DSC curve by which it can be readily identified. Thus, a highly paraffinic crude oil at an advanced stage of catagenic transformation shows a pronounced low temperature oxidation peak with a steep and high-ascending branch, a small-area right shoulder, and a smallish asphaltene oxidation peak, all shifted to low temperatures. This is due to the high content of normal paraffins and a low content of base oils and asphaltenes in such crudes.

On the contrary, naphthenic crude oils of low catagenic conversion rich in base oils and asphaltenes exhibit reduced heights and areas of the left shoulder of the first peak, a large-area right shoulder of the peak extending to temperatures as high as 420–440 °C, and a broad large-area asphaltene peak, all shifted to high temperatures. These regularities can be clearly seen in Fig. 2 where the TG-DSC curves of crudes of different chemical classes are presented. Their specific gravities are given in Table 1.

Table 1

Crude oils	Specific gravity, ρ_{15}^{15}
Caspian	0.8266
Eastern Sarutayussk	0.8627
Russian	0.9812
Western Siberian	0.9072
Urengoi gas condensate	0.7680
Vacuum gas oil	0.9625

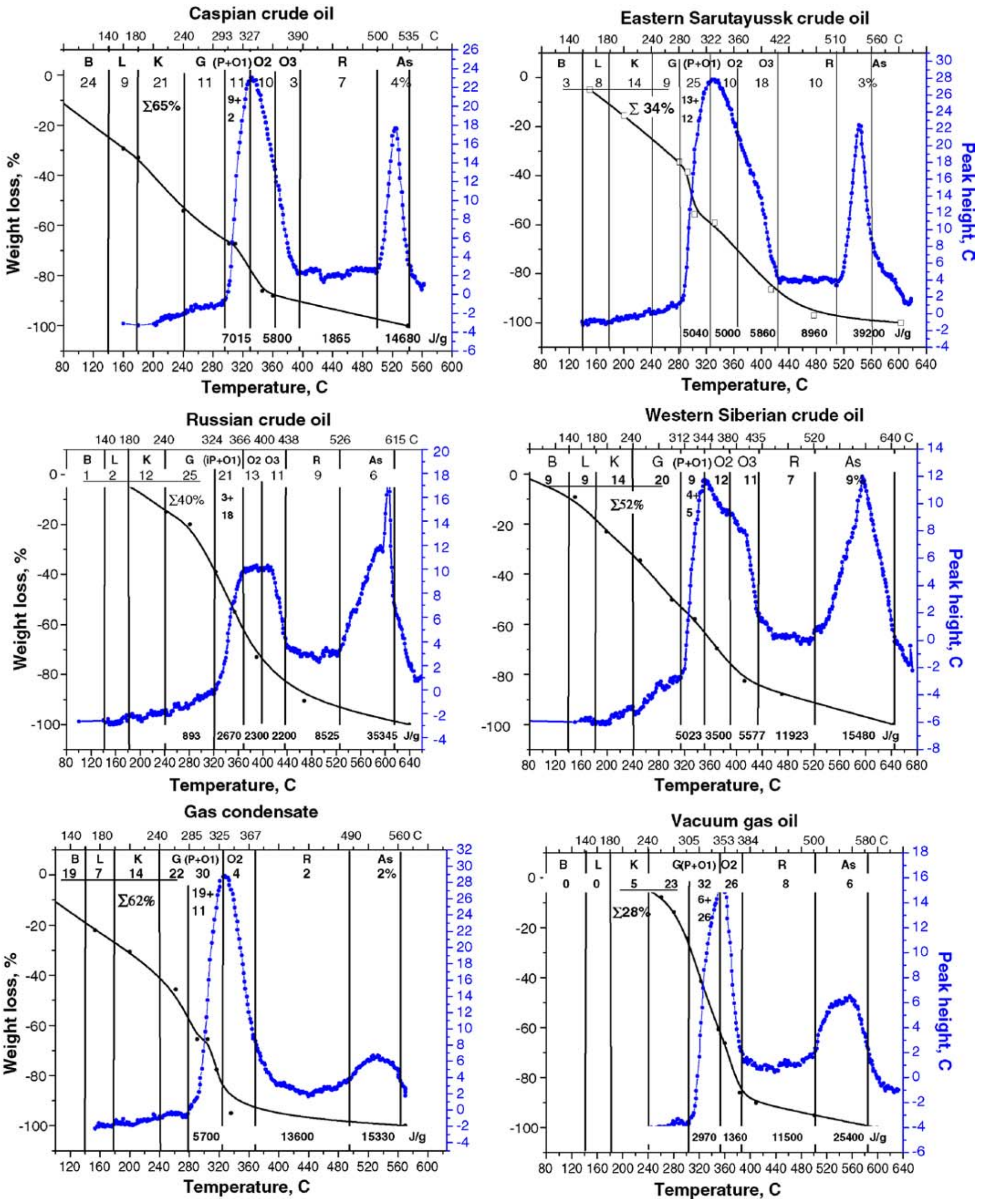

Fig. 2. TG-DSC curves of crude oils of different chemical classes: highly paraffinic Caspian crude, paraffino-naphthenic East Sarutayussk crude, naphthenic Russian crude, naphtheno-paraffinic Western-Siberian crude, Urengoi gas condensate and vacuum gas oil.

A definite correlation exists between the specific gravities of the samples and their component composition (see below):

(1) The light paraffinic Caspian crude has a large-distillate portion (65%) in which the benzine fraction predominates (24%) pointing to a high-catagenic conversion of this oil. It has a high content of normal paraffins (9%) with $T_{\mathrm{fl}} = 293\,^{\circ}\mathrm{C}$, little light base oil (2%), much more middle base oils (13%) and no heavy base oils. The content of resins and asphaltene is low (7 + 4 = 11%). The asphaltene peak is small and narrow with $T_{2\mathrm{st}} = 500\,^{\circ}\mathrm{C}$. These are the characteristic features of a highly aged (catagenically transformed) crude oil.

(2) The paraffino-naphthenic Eastern Sarutayussk crude oil contains besides normal paraffins (13%) also a fair amount of light (12%), middle (10%) and heavy (18%) base oils. Its asphaltene peak is small and narrow, very much as in the Caspian crude. The distillate portion is rather small (34%). The crude may be classed as of sapropel origin of low degree of catagenic transformation (it contains large amounts of base oils not transformed into distillate fractions).

(3) The naphthenic Russian crude contains no normal paraffins and little isoparaffins (3%), but appreciable amounts of light (18%), middle (13%) and heavy (11%) base oils. It has average amounts of distillate (40%), resin (9%) and asphaltene

(6%) components. It falls in the class of humus crude oils of average catagenic conversion.

(4) The naphtheno-paraffinic Western-Siberian crude contains little isoparaffins (4%) and appreciable amounts of light (6%), middle (12%) and heavy (11%) base oils. Compared with the Russian crude it has less light base oils (5%), the greater part of which has evidently transformed into the distillate, thus increasing its content to 52% (from 40% of the Russian crude), and it has practically the same amount of middle + heavy base oils and resins + asphaltene as the Russian crude.

(5) The Urengoi gas condensate (a very light crude oil) contains 62% of distillate, normal paraffins (19%) + light base oils (11%) 285–325 °C, middle or rather light base oil (4%) 325–367 °C, no heavy base oil, 2% of resins and 2% of condensed resins 490–540 °C and no asphaltenes. These are the common and expected values for gas condensates, which are the crude oils of the highest degree of catagenic conversion. Judging by the very low $T_{\text{fl}} = 285$ and $T_{\text{top}} = 325$ °C, the crude contains normal paraffins of low molecular mass of the type C18–C24 and little or no long-chain normal and isoparaffins. The practical absence of the right shoulder of the peak points to the absence of middle and heavy base oils in the crude.

(6) Vacuum gas oil contains 28% of the distillate of which 23% belongs to gas oil 240–305 °C, a large (P + O1) component (32%), of which only 6% belongs to the paraffins and 26% to the light base oil 305–353 °C, middle base oil 353–384 °C (26%), no heavy base oil, 8% of resins and 6% of condensed resins 500–560 °C. These are also the expected values for vacuum gas oils, in which high-boiling long-chain paraffins and low and middle boiling base oils should accumulate under the conditions of high-vacuum distillation.

3. Conclusions

(1) The proper choice of experimental conditions and the use of an updated version of DSC instrumentation coupled with loss weight measurements has allowed to gain a new and better insight into the nature of thermal reactions of petroleum hydrocarbons occurring in the temperature range 20–700 °C. Different oxidation mechanisms of progressively higher intensity have been established for paraffins + base oils, resins and asphaltenes oxidizing in the temperature intervals 300–400, 400–500 and 500–600 °C, respectively.

(2) Well resolved DSC oxidation peaks with clearly seen characteristic points have made possible the exact pinpointing of the temperature intervals of oxidation/evaporation of the crude oil components, and thus their quantitative determination via the TG curve.

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