

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.

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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. K ok 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. K ok 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

$$-\Delta H = KA_t \quad (1)$$

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

$$K = a + bT + cT^2 \quad (2)$$

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 T_2 is plotted on the X-axis and the differential temperature $T_1 - T_2$ on the Y-axis. The temperatures of transitions are indicated as intervals $T_{2in} - T_{2ip}$, where T_{2in} is the temperature T_2 where the DSC curve begins to deviate sharply from the baseline and T_{2ip} is the temperature T_2 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 T_{2ip} the reaction is largely over [10].

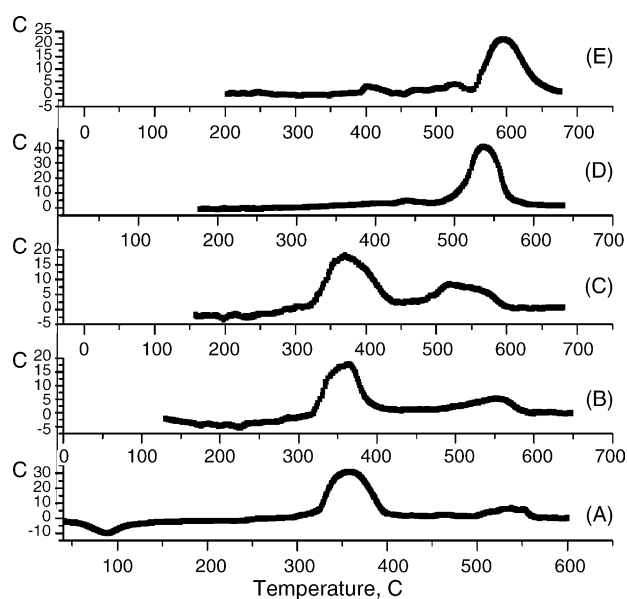


Fig. 1. DSC curves of various petroleum hydrocarbons: A, ceresin; B, medium base lubricating oil; C, heavy base lubricating oil; D, resin extracted from crude oil; E, asphaltene extracted from crude oil.

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