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APPLICATION OF THERMAL METHODS FOR THE ANALYSIS OF OILS AND OIL PRODUCTS

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ABSTRACT

TG, DTG and DTA were used for the study of qualitative and quantitative properties and thermal oxidation stabilities of oils and oil products. The paper reviews some of the methods which were applied in the Institute for Processing of Oil, USSR, for the study of oils. Characteristic parameters from TG-DTG curves were used to determine molecular masses and boiling points of paraffins and oils. They were also used for the determination of thermo-oxidizing stability of oils. Correlation was established between the composition of the oils and the shapes of the DTA curves.

INTRODUCTION

TG, DTG and DTA curves were successfully used for the determination of various properties of oils and oil products. In the present paper we are going to review and demonstrate some of the thermal analysis methods which were applied in the Laboratories of the Institue for Processing of Oil, USSR, in the affiliate of Moscow.

THERMOGRAVIMETRY AND DIFFERENTIAL THERMOGRAVIMETRY

Determination of molecular masses and boiling points

It was shown that TG-DTG curves can be used to determine physico-chemical characteristics of oils. There is a correlation between certain parameters in the TG and DTG curves of paraffins and their molecular masses [1]. Other physical properties of the paraffins which are related to their molecular masses, such as boiling points,

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can also be determined from the TG and DTG curves. For this purpose the TG-DTG curves should be recorded in an inert atmosphere (under a flow of nitrogen). Temperatures which correspond to weight losses of 10 or 25 percent (assigned by T_{10} and T_{25}, respectively) or DTG peak maxima (assigned by T_{max}) were taken as the parameters for the determination of the molecular masses and the boiling points. For example, the molecular mass, M, of a paraffin can be determined with any of the following equations:

$$M = 2.05\ T_{10} - 159.29 \tag{1}$$

$$M = 2.31\ T_{max} - 322.73 \tag{2}$$

The boiling point, T_b, of the paraffin can be determined with any of the following equations

$$T_b = 1.94\ T_{10} - 76.49 \tag{3}$$

$$T_b = 2.188\ T_{max} - 230.97 \tag{4}$$

In order to demonstrate these relationships, four different normal paraffin hydrocarbons were investigated by using a Setaram Thermal Analyzer in which the TG was recorded simultaneously with gas chromatography. The four hydrocarbons were hexadecane, (C_{16}), heptadecane, (C_{17}), eicosane (C_{20}) and tetracosane (C_{24}). Molecular masses of the four hydrocarbons were calculated with the help of equations (1) and (2) and data taken from the TG and DTG curves, respectively. The relative error of determination of the molecular mass ranged between 0.7 and 5.0%. Table 1 brings boiling temperatures taken from the literature [2] and values calculated with equations (3) and (4) with thermal data determined from TG and DTG curves, respectively. Deviations from literature data are less than 10°C.

TABLE 1

Boiling points of hydrocarbons taken from the literature and calculated from equations (3) and (4).

	Boiling points (°C)				
Hydrocarbons	From	Calculated			
	lit. [2]	Eq. 3	% rel.	Eq. 4	% rel.
Hexadecane (C_{16})	287.5	282.4	-1.8	287.7	+0.1
Heptadecane (C_{17})	303.0	305.7	+0.4	313.9	+3.6
Eiocosane (C_{20})	342.7	352.3	+2.8	344.6	+0.6
Tetracosane (C_{24})	394.0	387.2	-1.8	405.9	+3.0

The correlations which were established for normal paraffin hydrocarbons between parameters from TG-DTG curves and some of their physical properties were the basis for finding analogous

correlations for oil fractions of high-temperature boiling points. Four types of oil were studied for this purpose, IS-20 (b.p. 294-445°C), perfume oil (b.p. 300-442°C), VI-30 (b.p. 340-492°C) and IG-30 (b.p. 347-442°C). The following expressions were found applicable for calculating average molecular masses:

$$M = 2.381\ T_{10} - 252.32 \qquad (5)$$

$$M = 2.404\ T_{max} - 444.23 \qquad (6)$$

Calculated values of M obtained from the thermal analysis were in good agreement with experimental values obtained by cryoscopic molecular mass determinations.

Thermal oxidizing stability

Thermal analysis was used to determine criteria for the study of thermal oxidizing stability of mineral lubricating oils [3]. The following individual hydrocarbons were investigated, anthracene ($C_{14}H_{10}$), squalane ($C_{30}H_{62}$), hexadecane, ($C_{16}H_{34}$), tetracosane ($C_{24}H_{50}$) and various fractions from IS-20 and perfume oil, obtained by fractional distillation of these oils and showing different oxidizing stabilities. The stability depends on the chemical nature of the hydrocarbon. The following series of thermal oxidizing stability of hydrocarbons and oils is established from their chemical compositions: anthracene > tetracosane > squalane; hexadecane > tetracosane; IS-20 > Perfume oil.

The thermal analysis was carried out in an inert atmosphere (under the flow of He or N_2) and in an oxidizing medium (air or O_2). It was demonstrated that the TG curves of anthracene were almost independent on the medium, but weight losses and the velocities of weightloss, as well as the shapes of the TG curves of all other samples were dependent on the medium. The differences in behaviour depended on the chemical nature of the hydrocarbon.

The following criteria on the thermal oxidizing stability were established:

1. A stability parameter "K" characterizes the ratio between the temperature which corresponds to weight losses of 5, 10, 25 or 50% in an oxidizing environment (air) and the temperature which corresponds to the same weight losses in an inert atmopsphere (nitrogen).

2. Analogous for Activation energies, E, for the weightloss reactions were determined. Different activation energies were obtained for parallel reactions of the same samples if values were calculated from TG curves obtained in an inert atmosphere compared to those obtained in an oxidizing environment.

3. An index of thermo-oxidizing stability, I, was defined. In this index the stability parameter "k" of the examined oil or hydrocarbon is related to the stability parameters of the two standard hydrocarbons, the highly stable anthracene and the poorly stable squalane (anthracene-squalane standard), by the following equation

$$I = [(x-b) / (a-b)] * 100 \qquad (7)$$

in which a, b and x are "K" values of anthracene, squalane and that of the examined oil or hydrocarbon, respectively. Values for "K", E and I are shown in Table 2. They are in good agreement with reported data on increasing thermal-oxidizing stability series.

TABLE 2

Criteria of estimation of thermal oxidizing stabilities.

Hydrocarbon or oil	"K"	E	I
Hexadecane	0.995	2.51	80.3
Tetracosane	0.939	28.91	43.4
Anthracene	1.025	1.68	100.0
Squalane	0.873	51.54	0.0
IS-20	0.950	18.85	50.7
Perfume oil	0.893	42.32	13.2

During the investigation of natural oils and their hydrocarbons it was established that the different parameters of the TG-DTG curves follow an additive rule, (that is, the "K", E and I values depend on the various components of the natural oil and on the relative concentration of each component [4]).

DIFFERENTIAL THERMAL ANALYSIS

An attempt was made to broaden the potential of the DTA techniques for the study of oils and oil products. For this purpose the compositions of some of the fractions of the hydrocarbons in oils was determined by liquid chromatography. A correlation was found between the composition of the hydrocarbons and the shapes of the TG-DTG and DTA curves.

The location of the peak maximum in the DTA curve is also determined by the composition of the oil. If the oil contains a mixture of hydrocarbons, the DTA peak maximum, T_{max}, which characterizes the oil follows an additive rule [5] and can be calculated by the following addition equation:

$$T_{max} = (T_{max1}X_1 + T_{max2}X_2 .... + T_{maxn}X_n) / 100 \qquad (8)$$

where T_{max1}, $T_{max2} .... T_{maxn}$ are the peak temperatures for each of the hydrocarbons 1, 2...n, and X_1, $X_2 .... X_n$ are the concentrations of each of the hydrocarbons 1, 2...n, expressed in percentage.

It was established that the transition from paraffin naphthenes to aromatic hydrocarbons at the beginning of the first peak, as well as the maximum of this peak, shift to higher temperatures. However, the peak height and area diminish. The second peak, on the other hand, shows a greater area [5]. This is an indication for a greater thermal-oxidizing stability of the aromatic hydrocarbon compared to the aliphatic one.

There is a dependency between a specific dispersion, [F,C]y of the fractions of the hydrocarbons in oils, and the initial temperatures of the DTA peaks (X). A linear relationship occurs which can be expressed by the following equation:

$$y = 0.703X - 10.73 \qquad (9)$$

A coefficient of correlation of 0.96 was found for this case between y and the temperature of the beginning of the DTA peak [5].

The presence of resinous materials in the oil has an effect on the area of the second DTA peak. A linear relationship was established with a coefficient of correlation of 0.94 [5,6].

For the estimation of the qualitative composition of oil a criterion "K_a" was proposed (the criterion of aromatic hydrocarbons). "K_a" is defined as the ratio between the area of the second DTA peak and that of the first DTA peak. Values of "K_a" give information on the specific dispersion of the oil on the one hand and on the oil coking on the other hand. A linear relation was found between the values of "K_a" and the coking ability of the oil.

In conclusion, DTA, TG and DTG are useful tools for the study of qualitative and quantitative properties of oils as well as for the study of thermal properties of the oils.

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