

## **A STUDY OF THE HEAVY FRACTIONS AND RESIDUES FROM WEST SIBERIAN CRUDE OIL BY THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS TECHNIQUES**

*V. Penchev and M. Stojanova*

INSTITUTE OF ORGANIC CHEMISTRY, BULGARIAN ACADEMY OF SCIENCES,  
1040 SOFIA, BULGARIA

(Received November 11, 1987)

A method for comparing the thermochemical properties of high-boiling fractions and residues has been developed. The thermal effects vary in intensity and range, depending on the fractional and structure group compositions of the studied samples. Good agreement between DTA and TG data is observed. The thermal analysis of samples, obtained by liquid adsorption chromatography, reveals the specific differences of the individual structure group fractions in the processes of evaporation, thermal decomposition and coke formation. The observed effects are interpreted from the point of view of the different thermal stabilities and reactivities of the compounds contained in the chromatographic fractions. The results show that the TG-DTA method allows the quick determination of some characteristics depending on the group compositions of the high-boiling fractions and residues from West Siberian crude oil.

Thermoanalytic methods such as thermogravimetric analysis (TG), differential thermogravimetric analysis (DTG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have been widely applied to the investigation of mineral, inorganic and organic products in recent years [1-7].

These methods have also been used in the study of oil and oil products, as they allow the monitoring of phase transitions (melting point, boiling point, glass transition), thermal oxidation processes, processes of thermal decomposition, etc. The methods have likewise been applied successfully to the estimation of the thermal and oxidation stabilities of lubricants [5-9], in the investigation of the paraffin contents of diesel and jet fuels, and in the characterization of various lubricants.

During heating, oil and oil products undergo conversions which involve the emission or consumption of heat. The heat effects of the total reactions can be registered by DTA. Simultaneously, the changes occurring in the sample weight with time and temperature (TG) and the derivative thermogravimetric curve

(DTG) can be recorded. The different oil products can be characterized with respect to composition and physicochemical properties on the basis of their specific temperature curves.

In view of the large differences in the thermochemical properties and reactivities of the different hydrocarbon groups in the oil fractions, these methods may be expected to lead to useful and fast information. This information can be utilized for control of the processes of separation of the high-boiling oil fractions (deasphalting, solvent treatment, dewaxing).

We report here the results of a derivatographic investigation of a vacuum distillate, resulting from the atmospheric residue of West Siberian crude, and the products of the separation of a vacuum residue with selective solvents. We have tried to obtain relationships between the fractional and group compositions and the TG and DTA data.

## Experimental

The following fractions were obtained from West Siberian crude (Samotlor) by vacuum distillation: vacuum gas oil (VGO) with a boiling range of 623–813 K, and vacuum residue (VR). From the latter product, by extraction with light gasoline, asphaltenes (AS) are separated, and from the deasphalted oil (DA), by extraction with butane, tar-free deasphalted oil (TFDO) and tars (T) are obtained. The characteristics of the fractions are given in Table 1.

## Procedure

The derivatographic experiments were carried out on a MOM OD 103 system.

The preparation of the sample [4] involved a preliminary processing in a mixture with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at 453 K, leading to a constant distribution of the sample on the inert material. Next, the material was transferred into the derivatograph and the heating process was carried out under definite conditions.

Our investigations showed that the data depend strongly on the conditions of the experiment, and primarily on the type of crucible in which the sample is placed, the rate of temperature increase and the speed of the circulating gas. To obtain reproducibility of the results, the standard experimental conditions should be strictly observed. On the basis of preliminary studies, the experiments were carried out as follows: a mixture of 130 mg oil and 650 mg  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (ratio 1 : 5) was heated in a platinum crucible for 1.5 h at 453 K under an inert atmosphere. After cooling to room temperature, the crucible was transferred to the derivatograph and the oil

Table I Characteristics of West Siberian crude (Samotlor)

Sample	Density	Coking capacity	Pour point, K	Aver. MM	Elemental compos.				Metal cont. $\times 10^{-2}$			Group composition		
					C	H	S	N	V	Ni	par./naph.	arom.	tars	
0.9164	0.94	—	391		86.4	12.2	2.2	0.2	tr.	tr.	52.83	50.3	—	
VR	1.0168	19.7	314	827	86.0	10.3	2.7	0.6	1.7	0.8	6.07	32.5	49.3	
DA	0.9964	13.9	302	751	85.2	10.7	2.7	0.5	0.8	0.1	13.93	56.9	29.1	
TFDO	0.9714	7.5	301	739	85.5	11.2	2.5	0.3	0.2	0.1	11.5	79.9	8.6	
T	1.0775	27.6	345	907	86.4	9.5	3.0	0.8	2.2	1.1	2.3 <sup>a</sup>	92.3 <sup>b</sup>	7.3	
AS	1.0859	46.7	439	1484	87.5	8.3	2.8	1.1	6.4	3.2	1.9 <sup>c</sup>	63.8 <sup>d</sup>	36.1	

<sup>a</sup> Four fractions are eluted; a solution of 97% DEE and 3% ethanol is used;

<sup>b</sup> three fractions are eluted; extraction with pyridine;

<sup>c</sup> four fractions are eluted; extraction with a solution of 97% DEE and 3% ethanol;

<sup>d</sup> three fractions are eluted; the extraction with pyridine.

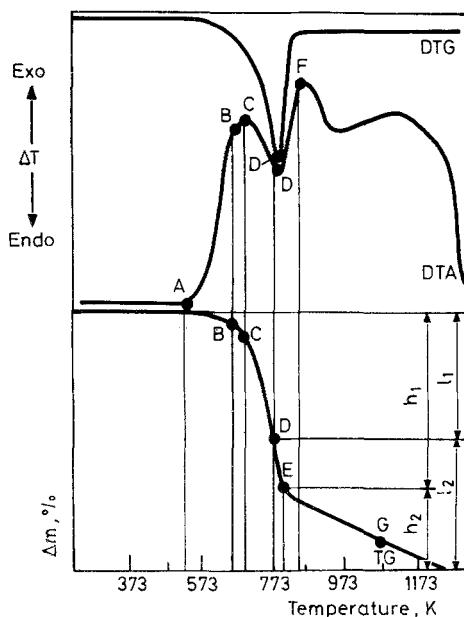


Fig. 1 DTA, DTG and TG curves of TFDA in air

sample weight was determined exactly.  $\alpha\text{-Al}_2\text{O}_3$  was introduced into the reference crucible. Quartz test-tubes were placed upside down on the reference and measuring platinum crucibles to cover them. Argon or air was admitted to the tube situated over the measuring crucible, at a rate of 5–6 l/h. The experiments were performed under the following conditions: sensitivity of TG 200, of DTA measurements 1/5, of DTG measurements 1/10, and rate of temperature rise 10 deg/min.

## Results and discussion

### *Thermal studies in air*

With a programmed increase of temperature, interrelated complex processes differing in character and producing a series of heat effects (visible in the DTA curves) proceed in the oil fractions under investigation. Figure 1 presents the DTA curves of the TFDO. The curves of the other samples are similar.

All samples investigated in the presence of air showed pronounced exothermic behaviour in the DTA curves, which had several maxima (the first, of them at 623–723 K; point C) and a minimum (point D, which coincided with an extremum in the DTG curve). A sharp decrease in weight was observed in the TG curve within

the range between two exothermic effects (points C and E). Irrespective of differences in fractional and chemical group compositions, the first exothermic effect is observed at nearly the same temperature (about 513 K). Comparison of the weight changes at the temperature where the first exothermic effect begins shows no substantial weight losses. The beginning of the exothermic effect (point A) indicates the beginning of thermal oxidation reactions accompanied by destruction. 513 K was assumed to correspond to the beginning of the process because determination of the latter on the basis of the DTA curves is not reliable. The weight change at this point is negligible and its exact determination is difficult. Accordingly, we also took into account the temperature corresponding to a 5% weight loss, since it is characteristic of each sample and depends on fractional and chemical group compositions (Table 2).

The data obtained at the temperature of 5% weight loss (point B) are very interesting. For the VGO, this loss occurs at 593 K. For the VR and the fractions obtained from it, 5% weight losses are attained at 653–713 K. The TFDO shows the lowest temperature of 5% weight loss, while for the AS fraction this temperature is 713 K. In view of the fact that the fractions differ as concerns the molecular masses of the different components (which in this case is very important), one can assume that the fragments obtained from the AS fraction during thermal oxidation are small (short-chain substituents being present), so that their elimination has no essential effect on the sample weight.

The first exothermic maximum in the DTA curve corresponds to the temperature region where thermal oxidation destruction (cracking) prevails over thermal cracking. This maximum may represent the percentage of structures that are easily destroyed during thermal oxidation. The VR fractions have close temperatures of thermal oxidative cracking (683–693 K), the only exception being the AS (723 K). This can be ascribed to the structural peculiarities of the AS components, which have a higher stability towards thermal oxidation. Simultaneously, it should be noted that the largest weight losses at point C correspond to the TFDO (9.4%) and DA (7.1%), which confirms our assumption as to the formation of fragments with larger masses under these conditions. This conclusion is also confirmed by the data on the VGO, which has the lowest temperature of the exothermic maximum (633 K), along with the largest weight loss (17%).

The endothermic minimum deserves special attention. It coincides with the extremum in the DTG curve and is situated in the region of sharp weight loss. The endothermic minimum is at almost the same temperature (763–773 K) for all VR fractions. However, the weight losses are quite different. The fraction with the lowest T and AS contents (TFDO) shows the highest weight loss (54%), whereas a loss of 24% is observed for the AS. This indicates that the endothermic minimum can characterize the content of easily cracking components such as oils and, above

Table 2 Results obtained in air

Sample	Wt. loss at 513 K	Temp. of % wt. loss, K	Selected characteristic points (weight losses)										Residue	
			exo-eff., I		endo-eff.		break-point		$l_1/l_2$	$h_1/h_2$	Exo-eff., II		1073 K	1273 K
			temp., K	wt. loss, %	temp., K	wt. loss, %	temp., K	wt. loss, %			temp., K	wt. loss, %		
VGO	0.8	593	633	16.9	713	58.5	763	83.0	1.45	4.9	793	86.0	—	—
VR	0.8	663	683	6.9	763	44.9	793	61.0	0.80	1.6	823	65.0	17.0	2.3
DA	0.8	663	673	7.1	773	50.4	793	62.2	0.76	1.7	833	66.9	15.7	1.6
TFDO	0.4	653	693	9.4	773	53.9	803	69.5	1.2	2.4	843	73.4	8.6	—
T	0.4	673	693	7.0	763	31.2	803	44.5	0.5	0.8	833	47.6	33.6	14.1
AS	0.4	713	723	7.9	763	23.6	803	34.6	0.3	0.5	833	38.6	44.1	27.6

all, oils containing paraffinic-naphthenic hydrocarbons with uncondensed rings. For the VGO, this endothermic minimum is found at 713 K and corresponds to a considerable weight loss (58%), which is associated with both the fractional and chemical group compositions (a high concentration of paraffinic-naphthenic hydrocarbons).

The next exothermic effect can be attributed to polycondensation processes leading to primary coke formation. It should be noted that for VR fractions this effect is observed within a narrow temperature range (823–843 K). The conclusion as to primary coke formation due to polycondensation is confirmed by the change in slope of the TG curve, which is accompanied by a changing rate of weight loss. The change in slope of the TG curve determines a breakpoint (point E), where the weight losses correlate with those corresponding to the second exothermic effect. Table 2 shows the largest loss for the TFDO (73%), i.e. for the fraction with the lowest concentration of polycyclic aromatic hydrocarbons and tars. The weight loss data concerning T and AS (48% and 38%, respectively) indicate the predominance of polycondensed structures. This is also confirmed by the results on the VGO, for which point E is found at 793 K, the weight loss reaching 86%. Obviously, the low tar, and polycondensed aromatic hydrocarbon concentrations in the distillate fraction favour the formation of a small amount of coke.

The amount of coke formed (including that partially burnt) is estimated at 1073 K. The data obtained are in good agreement with those obtained by the method of Conradson. In the VGO, where the content of polycondensed aromatic structures and tars is low and asphaltenes are practically absent, no coke is established at 1073 K. Hence, it may be assumed that the coke is burnt due to the presence of oxygen. This can be established by evaluating the coke residue at 1273 K. Hydrocarbon residues at this temperature are negligible, and inorganic admixtures predominate. For this reason, the largest amount of inorganic residues is found for the AS (28%), followed by T (14%) and the VR (2%), no such residues being found in the TFDO.

#### *Thermal studies in an inert medium (argon)*

Experiments carried out in an inert medium related to the thermal stability of the fractions under conditions excluding the occurrence of thermal oxidation reactions. For this reason, high-purity argon (99.9%) was used. To eliminate possible oxygen traces, the argon was passed through adsorbers containing a nickel catalyst and Pt-Al<sub>2</sub>O<sub>3</sub>. No essential differences in the thermal curves of the initial and additionally purified argon were observed. For this reason, the argon was not subjected to additional purification.

The thermal curves (Fig. 2) of the samples investigated have similar shapes,

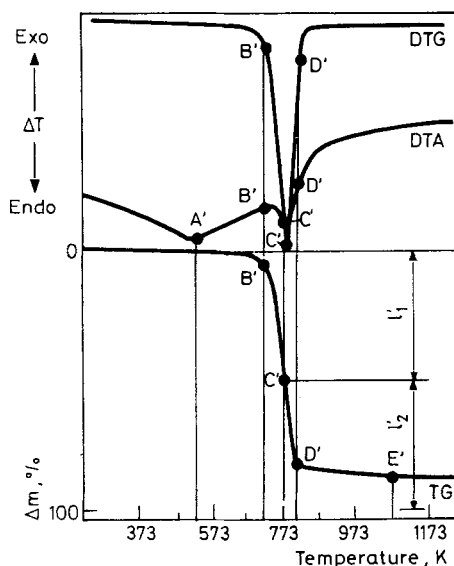


Fig. 2 DTA, DTG and TG curves of TFDO in argon

characterized by a distinct endothermic peak (743–773 K), which corresponds to intensive thermal cracking. The latter is confirmed by the DTG and TG regions of quick weight losses. This endothermic effect is followed by a series of weak exothermic effects, forming a broad plateau. Thermal condensation processes leading to coke formation can be assumed to proceed in this region. To interpret the data on the curves obtained, we considered the following points: *A'*, weight loss at 513 K; *B'* and *D'*, beginning and end, respectively, of the endothermic effect, which in each experiment coincided with the extremum of the DTG curve. In addition, the

Table 3 Results obtained in an inert medium

Sample	Wt. loss at 513 K	Temp. of 5% wt. loss, K	Characteristic endotherm eff.		Break-point		Residue		
			temp., K	wt. loss, %	temp., K	wt. loss, %	1073 K	1273 K	
VGO	0.8	593	743	70	773	84	3.6	4.2	2.5
VR	1.5	713	773	44.6	823	71	0.8	25.4	23.1
DA	1.5	713	773	47.2	823	76	0.92	17.3	15.0
TFDO	—	713	773	50	813	82.3	1.2	13.1	12.3
T	0.8	703	763	43	813	66	0.76	29.2	26.9
AS	—	723	773	29	823	46	0.41	48.5	46.1



temperature of 5% weight loss and the amount of coke at 1073 K and 1273 K were taken into consideration. The results are given in Table 3.

The weight loss at 513 K is 0.8% for the VGO, and reaches 1.5% for the remaining samples. Comparison of the weight losses for the same samples treated in air and in an inert medium, respectively, shows losses about twice as high in the latter case. This difference cannot be attributed to solvent residues or inaccurate rectification. Evidently, the gas medium exerts some effect during thermal treatment. Oxygen-containing compounds are probably formed at these relatively low temperatures on the action of oxygen, and these compounds retain part of the oxygen in the liquid phase after thermal destruction.

It should be pointed out that the temperatures of the endothermic peak during experiments with argon are very close to those established in air for the same endothermic minimum. Comparison of the weight losses at these points (*B'* and *D*) shows that in an inert medium the bulk of the sample passes into the vapour phase. This is probably due to the formation of thermally stable oxygen-containing compounds, as mentioned above. It should be emphasized that the sample sequence according to weight loss in an inert medium is the same as in air.

The amount of coke formed at 1073 K is several per cent higher than that established by the method of Conradson. This is not unexpected in view of the fact that the conditions of derivatographic experiments suppress the oxidizing effect of oxygen. The amount of coke formed under argon at 1273 K is only a few per cent lower than that obtained at 1073 K. This confirms the above conclusion about the intensive burning of coke in air at 1073–1273 K.

#### *The rôle of the chemical nature of the samples investigated*

Our thermal studies have shown that the fractional and chemical group compositions of the samples strongly affect the intensity of thermal destruction reactions and coke formation. The thermal effects of these reactions could be used as quantitative criteria for the degree of their occurrence. Unfortunately, the apparatus used in our studies does not allow an exact calibration on the basis of which calculation of the thermal effects would be possible. To avoid these difficulties, Sevecek et al. [10] have applied an indirect method for investigations of the thermal destruction of polymers, using the ratio  $h_1/h_2$  determined by the two stages of the weight loss process.

Our TG curves for heavy fractions and the VR from West Siberian oil have shown two interesting points: *D* and *C'* (in air and in an inert medium, respectively), which correspond to the minimum of the endothermic effect; and the break-point (*E* and *D'*), which corresponds to the beginning of coke formation. The

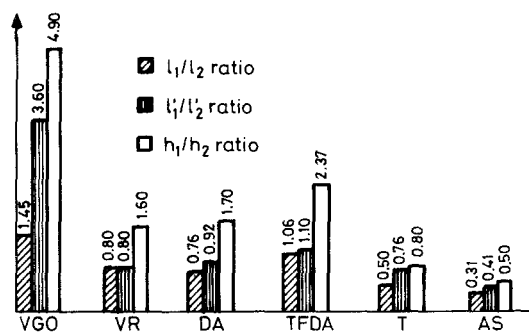


Fig. 3 A schematic diagram of the characteristic ratios  $l_1/l_2$ ,  $l'_1/l'_2$  and  $h_1/h_2$

corresponding ratios  $l_1/l_2$  and  $h_1/h_2$  are important characteristics of each sample (Fig. 3).

The data concerning point *E* show that oil-rich fractions have a ratio  $h_1/h_2$  of more than 1. The points determined with respect to the endothermic minimum (*D* and *C'*) show that a ratio  $l_1/l_2$  of more than or equal to 1 corresponds to oil fractions with low tar and asphaltene contents, whereas for T and AS this ratio has considerably lower values (0.5 and 0.3, respectively). Comparison of the ratio  $l_1/l_2$  (air) with the ratio  $l'_1/l'_2$  (argon) shows that the value  $l_1/l_2$  is always higher than or equal to the value of  $l'_1/l'_2$ . This is due to the fact that the amount of volatile products evolved is higher in cases when argon is utilized.

The ratios  $l_1/l_2$  and  $h_1/h_2$  correlate well with the values obtained on coke formation. Hence, these quantities can be used to estimate the coking capacity of a given oil sample, which is an indirect indication of its chemical group composition (the boiling points of the fractions being equal).

Parallel thermal studies in air and in inert gas ensure a better interpretation of the data and reliable conclusions on the hydrocarbon group compositions.

## Conclusion

The experiments performed showed that useful information on the thermal oxidation stability and thermal cracking of oil products can be obtained by thermal studies. On this basis, reliable conclusions can be drawn on the chemical and structure group compositions of oil samples. In addition, the technological processes of mineral oil production can be controlled.

## References

- 1 F. Al-Sammerrai and D. Al-Sammerrai, *Thermochim. Acta*, 94 (1985) 295.
- 2 S. H. Al-Madfai, D. A. Al-Sammerrai and M. M. Barbooti, *J. Therm. Anal.*, 29 (1984) 1123.
- 3 S. M. Dyszel, *Thermochim. Acta*, 38 (1980) 299.
- 4 G. G. Valjavin, E. V. Artamonova and N. I. Vetoshkin, *Sb. nauch. tr. BashNII po pererab. nefiti*, 16 (1977) 54.
- 5 M. Wesolowski, *Thermochim. Acta*, 91 (1985) 265.
- 6 F. Noel and G. Granton, *American Laboratory*, (1979) 27.
- 7 F. Babaev and G. Ovanesova, *Dokl. AN AzSSR*, 37(8) (1981) 57.
- 8 G. Naumova et al., *Khim. tv. topliva*, 6 (1975) 70.
- 9 D. E. Diskina, I. M. Tiunova, K. M. Badishtova, E. B. Ivankina, N. I. Grigoreva and E. E. Obmochaeva, *Neftepererab. i neftekhimia*, 2 (1978) 12.
- 10 P. Sevecek, V. Roubicek et al., *Thermochim. Acta*, 93 (1985) 321.

**Zusammenfassung** — Ein Verfahren zum Vergleich der thermochemischen Eigenschaften von schwersiedenden Fraktionen und Rückständen wurde entwickelt. Die thermischen Effekte unterscheiden sich in Intensität und Bereich des Auftretens, immer abhängig von der chemischen und strukturellen Zusammensetzung der Proben. Zwischen DTA- und TG-Daten konnte gute Übereinstimmung beobachtet werden. Die Thermoanalyse der durch Adsorptionsflüssigkeitschromatographie erhaltenen Proben offenbart die spezifischen Unterschiede der einzelnen strukturellen Fraktionen während des Verdampfungs-, thermischen Zersetzungs- und Verkokungsprozesses. Die beobachteten Effekte wurden unter Gesichtspunkten der unterschiedlichen thermischen Stabilität und Reaktivität der aus den chromatographischen Fraktionen gewonnenen Verbindungen diskutiert. Die Ergebnisse zeigen, dass das TG-DTA-Verfahren eine schnelle Bestimmung einiger von der funktionellen Gruppenzusammensetzung abhängigen Eigenschaften schwersiedender Fraktionen und Rückstände aus westsibirischem Rohöl ermöglicht.

**Резюме** — Развѣт метод для сравнения термохимических свойств высококипящих фракций и остатков сырой нефти. Термические эффекты меняются как по интервалу, так и интенсивности в зависимости от фракционных и структурно-групповых составов изученных образцов. Наблюдалось хорошее согласие между данными ДТА и ТГ. Термический анализ образцов, полученных с помощью жидкостной адсорбционной хроматографии, показывает специфические различия отдельных структурно-групповых фракций в процессах испарения, термического разложения и образования кокса. наблюдаемые эффекты интерпретированы на основе различной термической устойчивости и реакционной способности соединений, содержащихся в хроматографических фракциях. Результаты показали, что метод ТГ-ДТА позволяет быстрое определение некоторых характеристик в зависимости от группового состава высококипящих фракций и остатков западно-сибирской нефти.