Available online at www.sciencedirect.com
SCIENCE DIRECT®

Thermochimica Acta 444 (2006) 26–34

thermochimica acta

www.elsevier.com/locate/tca

The effect of sample mass and heating rate on DSC results when studying the fractional composition and oxidative stability of lube base oils

Yu.L. Shishkin

Gubkin Russian State University of Oil and Gas, Leninski Prospect 65, 119991 Moscow, Russia

Received 15 January 2006; received in revised form 30 January 2006; accepted 6 February 2006
Available online 6 March 2006

Abstract

The method of dynamic microdistillation instrumented through DSC has been further elaborated and validated using distillate and residual base oils as model systems. The two major experimental factors of the method—sample mass and heating rate were varied to determine the optimal (standard) experimental conditions for better fraction resolution and thus more reliable quality assessment of petroleum products (lube oils). If these are increased, the fraction resolution ability of the method is reduced—the lighter fractions evaporate at temperatures close to those of the heavier ones, and generally all the fractions evaporate/oxidize at higher temperatures. Two major types of reactions in the heated sample were identified—the one occurring on the metal surface of the crucible leading to a polymer (lacquer) film formation and the other the oxidative cracking in the bulk of the sample leading to the formation of gaseous products. The extent of the lacquer film formation on the crucible metal surface can be reduced by increasing the heating rate and/or the sample mass, while their reduction results in better fraction resolution.

Keywords: Base lube oils; Differential scanning calorimetry; Fractional analysis

1. Introduction

Thermal methods of analysis (DSC, DTA, TGA) have found wide application for studying various physico chemical properties of petroleum derived products, among which the stability of lubricating oils to oxidation under various conditions occupies a prominent place. Kowalski [1] using pressurized DSC found a drastic reduction of oxidative stability of engine oils by admixture of vegetable oils due to easier initiation of the free radical promoted auto oxidation of vegetable oils. Perez [2], using the same method, studied the adverse effect of additives depletion by methanol fuels on the stability and volatility of commercial lubricants. Karacan et al. [3] studied the dependence of thermal stability of engine lubricant on the usage period. It was found that as the usage period increases the molecular weight of the lube oil also increases and some residue type components, which can only be destroyed at very high temperatures, are produced in the oil phase. The probable mechanism is the peroxide radical formation and C–C bond scission producing volatile and high molecular weight products (resins) [4]. The effect of oil composition on the pyrolysis and combustion kinetics was studied in [5]. DSC and TGA techniques were used in [6,7] to study oxidation and pyrolysis behavior of whole crude oil and its SARA fractions separated by column chromatography. Temperature intervals of evaporation and oxidation of each fraction were established and an important observation made that each fraction in whole crude oil follows its own reaction (distillation and cracking) pathway independent of the presence of other fractions. This finding points to the possibility of using DSC–TGA for the quantitative fractional analysis of crude oils and petroleum derived products. In line with this result it was shown in [8,9] that DSC and TG oxidation curves with their characteristic profiles reflect (are conditioned by) the chemical composition of the sample. It is known [10] that the lubricant fraction of petroleum contains mono-, bi-, and tri(cyclic) naphthenes, mono-, bi- and trinaphthenomonoaromatics, iso- and in lesser amounts normal paraffins, etc. These compounds have different molecular masses and boiling points. The central postulate of the method of dynamic microdistillation (MDM) [9] is that on heating a complex mixture under conditions of free gas exchange, often realized in DSC or TG experiments, the lighter fractions will leave the sample first, and the heavier ones second, at progressively higher

---

E-mail address: yu.l.shishkin@mail.ru.

0040-6031/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2006.02.015

temperatures proportional to their molecular masses and boiling points.

In TG–DSC experiments small sample masses (3–15 mg) and flowing inert or oxidative atmospheres are usually used. The sample has the form of a thin layer in close contact with the bottom of a metal sample pan. In case the pan has no covering lid, diffusion of gases from and to the sample is greatly accelerated due to good convection, the temperature gradients within the sample are minimal, and this enables the fractions of different volatility to leave the mixture consecutively at temperatures close to (but lower than) their saturation ones as the temperature of the sample is raised at some constant rate. To distinguish this method of distillation from the conventional one where great sample masses are used and evaporation takes place in closed environment at boiling temperatures of the mixture it should have its own name, and the term "dynamic microdistillation" seems to be appropriate.

Thus, the method's essential features are: (i) dynamic heating regimes; (ii) dynamic oven atmospheres (flowing ones or natural convection); (iii) small sample masses, enabling thin layer evaporation and ensuring minimal concentration and temperature gradients within the sample. These are the conditions, besides those pertaining to the construction of the calorimetric cell [11,12], for obtaining reliable TG–DSC experimental results amenable to plausible interpretation and quantification.

In studying lube oils by DSC the sample loaded pan (crucible) can be viewed as a micro reactor in which chemical reactions occurring on the lubricated metal surfaces of a car engine can be modeled and monitored. The effect of inert or oxidative atmospheres, temperature regimes and usage time on the stability of the material and hence its exploitation properties can be studied via DSC and TGA experiments. High-resolution calorimetry was used [8,9] to achieve a better understanding of the thermal properties of crude oils of various chemical classes (origin). Experimental conditions necessary for obtaining reliable DSC data had been specified. In the present communication a further step in this direction is made by giving a more close attention to such important factors of the DSC experiment as the sample mass and the heating rate.

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 without recourse to specially organized oven gas flow. Lube oils (3–15 mg) in a crucible of said dimensions form a thin layer and evaporate on heating at temperatures lower than those of boiling. Due to good convection and reduced diffusion resistance, the vapors and gases escape from the sample 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 20, 45, and 70 °C/min were used. Total heat effects ΔH_t/J of thermal reactions were calculated using the formula:

$$-\Delta H_{\mathrm{t}} = KA_{\mathrm{t}}. \qquad (1)$$

The heat transfer coefficient K dependence on the temperature above $T = 0$ °C was approximated by the formula:

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

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 $a = 3.04$, $b = 9.12 \times 10^{-4}$, $c = 4.9 \times 10^{-5}$. The relative standard deviation (R.S.D.) for 5–6 measurements in the interval 20–700 C using formulas (1) and (2) was estimated to be 5–10%.

3. Results and discussion

Lube base oils obtained from the light and middle crude oil distillates and a heavy residual base oil were studied. Their technical properties are given in Table 1.

A typical DSC curve of a light lube base oil as recorded by the instrument (screen copy) and its presentation in the Deconvolution module of the program Thermo are given in Fig. 1A and B. The upper curve with bumps on it is the temperature of the sample T_1 and the lower straight line is that of the reference material (crucible) T_2.

In high-resolution calorimetry it is very important for the instrument to have a practically ideal base-line in the temperature interval of the heat transitions measured, which for petroleum hydrocarbons often extends over 300–400 °C. It can be seen from Fig. 1A that this condition is satisfied in the present method. In fact, the deviation of the T_2 temperature from the straight line nowhere along the line exceeds 1 °C, and the straight baseline T_{base} drawn under the peaks from 200 to 560 °C practically coincides with the T_2 curve. Thus, small heat effects generating $\Delta T = T_1 - T_{\mathrm{base}} > 2$ °C can well be resolved and no spurious or distorted heat effects are likely to be registered.

The curves in Fig. 1 show that there are at least four regions on the temperature scale of the DSC run where thermal events of different nature occur in the heated sample. These are more clearly seen in Fig. 1B, in which the temperature T_{base} of the

Table 1
Technical parameters of distillate and residual lube base oils

Parameter	Light distillate base oil 350–420 °C	Middle distillate base oil 420–500 °C	Heavy residual base oil >500 °C
Kinematic viscosity (mm^2/s) at 40 °C	30	66	243
Density at 20 °C ($\mathrm{g/cm}^{-3}$)	0.8411	0.9090	0.9390
Pour point (°C)	−7	−3.5	−4.6

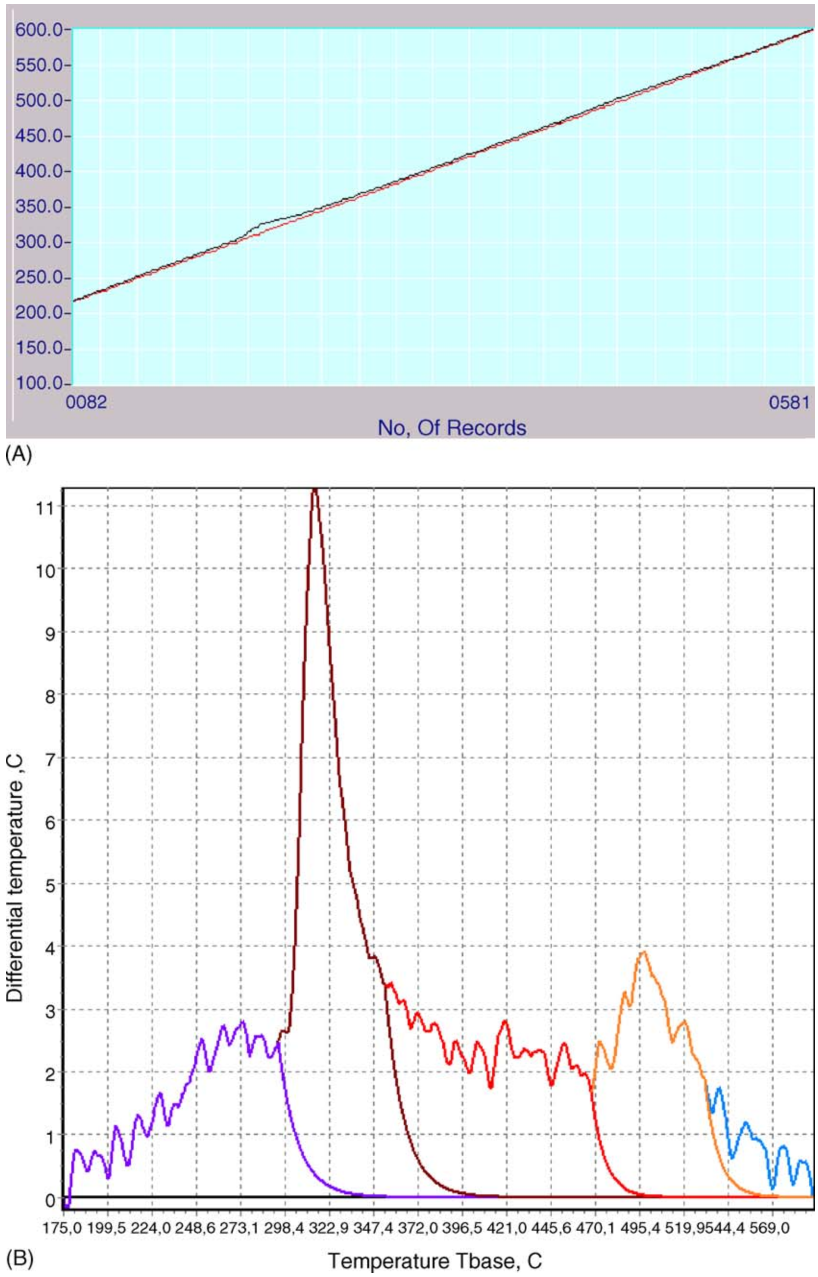

Fig. 1. (A) DSC curves of light distillate base oil 350–420 °C as recorded by the instrument (screen copy); (B) DSC curve as seen in the Deconvolution module of program Thermo. Sample mass $M = 0.0032$ g, heating rate $V = 45$ °C/min.

base-line is plotted on the X-axis and the differential temperature ΔT is plotted on the Y-axis. Here, exothermic effects of varying intensity are separated from one another by exponential curves (deconvoluted), mimicking the tail branches of DSC peaks, and thus four sub-peaks are generated on the otherwise continuous exothermic peak extending from 180 to 530 °C. The peak deconvolution procedure is described in greater detail in [8].

From about 180 °C fuming of the sample begins and from Fig. 1B one can see that this process is accompanied by oxidation of low intensity (of low heat and kinetics). At 294 °C, the heat evolution sharply increases, causing appearance on the DSC curve of a large exothermic peak. Apparently, oxidation mechanism changes at this point—solid paraffins C–C bonds begin to form peroxides, whose subsequent decomposition leads to reactive free radical chain formation and propagation accompanied by high heat and explosion-like kinetics. The ascending branch (left shoulder) of the peak can thus be associated with oxidation/distillation of predominantly paraffinic fractions of the base oil, and its descending branch (the right shoulder)—with oxidation of naphthenic (more oily) fractions of the sample proceeding with lower heats and kinetics.

On further heating aromatic fractions with condensed aromatic and/or naphthenic rings begin to oxidize and evaporate in the interval 350 (400)–500 (520) °C. Data obtained by adsorption column chromatography shows the following sequence of hydrocarbon fractions eluted from the column: paraffinonaphthenes, monocyclic aromatics, bicyclic aromatics, polycyclic aromatics (resins), asphaltenes, carbines (the latter two are absent in unused base oils). It would be safe to assume that the same sequence is maintained in the case under consideration. Then the following approximate assignment of HC fractions to the temperature scale of DSC run can be proposed.

(1) Heavy gas oil fraction retained in the distillate base oil: 180–280 (320) °C
(2) Naphthenoparaffinic fraction (base oils+paraffins): 280–350 (400) °C.
(3) Monocyclic aromatics to which the lower portion of the descending branch of the main peak may be allocated.
(4) Bi- and polycyclic aromatics oxidizing in the interval 380 (400)–450 °C.
(5) Closely packed polycyclic aromatics (hard lacquer resins) with oxidation temperatures above 450 °C and lower than 520 °C.
(6) Asphaltenes and carbines oxidizing above 520 °C.

In Fig. 1B the first and second sub-peaks correspond to fractions 1 and 2, respectively; fractions 3 and 4 are combined in sub-peak 3, and sub-peak 4 refers to fraction 5.

It is worthy of note that the packed aromatics (lacquer resins) oxidize with very high heats, causing a second sharp exothermic peak on the DSC curve. Evidently, a new oxidation mechanism of higher intensity sets in when temperatures 450 °C or higher are reached. This may be due to the fact that when strong intermolecular interactions in closely packed long-chain resin structures are overcome, the freed molecules find themselves at temperatures sufficiently high for the most stable C–C and C–H bonds to be broken, and thus a large number of small oxidized species are formed, generating heat which is proportional to their number. The same applies to the asphaltene and other high molecular closely packed hydrocarbons.

The results presented so far have been obtained for definite experimental conditions and are valid for these conditions and no others. It is not clear whether they are optimal for, say, the fraction separation, and what in general is the dependence of DSC results on such factors as the sample mass and/or heating rate. Below these issues are addressed in some detail.

The sample size (form, manner of packing in the crucible) and heating rate are the major experimental factors influencing the results obtained by MDM (besides others discussed above). One might expect that too great heating rates would lead to crowding of fractions and overlapping of peaks while too low ones would lead to poor fraction resolution due to peaks becoming too low and spread out (and loss of volatile fractions at temperatures below the oxidation region, making them invisible by the calorimetric method). Likewise, too great sample masses may increase diffusion resistance and hinder fractions consecutive release from the mixture, while too low ones will reduce the sensitivity of the method. It would be of interest to find out what are the actual values of these two factors for optimal HC fraction separation as reflected in the position, size, and shape of the corresponding peaks on the DSC curve. To this end a number of experiments described below were conducted.

First the heating rate was kept constant and sample masses were varied, and then heating rates were varied while the sample mass was kept constant. The position and shape of peaks on the DSC curve—temperatures and breadths of sub-peaks and relative heats associated with each fraction (sub-peak) were noted as functions of the chosen variables. The results obtained are summed up in Tables 2 and 3 and Figs. 2 and 3.

Table 2
Dependence of temperatures and relative heats of oxidation of lube oil fractions (DSC sub-peaks) on sample mass at a constant heating rate $V = 45\,^{\circ}$C/min

Number	Fraction	Sub-peak temperatures $T_{st} - T_{end}$ (°C)			α_1	α_2	α_3
	Sample	$M_1 = 3.2$ mg	$M_2 = 11$ mg	$M_3 = 15$ mg	M_1	M_2	M_3
350–420 °C distillate lube oil							
1	Gas oil	180–294	260–303	270–287	13.80	2.80	0.27
2	Naphthenoparaffins	294–354	303–353	287–374	31.10	65.1	83.4
3	Mono/bi/poly cyclic aromatics	354–468	353–452	374–455	27.33	24.6	14.0
4	Lacquer resins	468–531	452–484	455–503	27.80	7.53	2.40
Number	Sample	$M_1 = 3.2$ mg	$M_2 = 10.6$ mg	$M_3 = 16$ mg	M_1	M_2	M_3
420–500 °C distillate lube oil							
1	Gas oil	220–306	233–293	270–293	5.84	4.0	1.4
2	Naphthenoparaffins	306–363	293–376	293–402	37.3	56.4	60.8
3	Mono/bi/polycyclic aromatics	363–464	376–485	402–505	19.9	25.1	23.3
4	Lacquer resins	464–528	485–558	505–557	37.0	14.5	14.6
Number	Sample	$M_1 = 3.4$ mg	$M_2 = 10.6$ mg	$M_3 = 15$ mg	M_1	M_2	M_3
Residual lube base oil							
1	Gas oil	240–322	260–307	260–309	4.90	1.90	1.90
2	Naphthenoparaffins	322–408	307–432	309–447	33.9	60.1	58.5
3	Mono/bi/polycyclic aromatics	408–470	432–498	447–491	10.6	10.6	8.20
4	Lacquer resins	470–544	498–580	491–543	50.6	27.4	31.4

Table 3
The heating rate dependence of temperatures and relative oxidation heats of the four lube oil fractions (sub-peaks) of distillate and residual base oils; sample mass $M = 11–12$ mg

Number	Fraction	Sub-peak temperatures $T_{st} - T_{end}$ (°C)			Relative oxidation heats		
		20[a]	45[a]	70[a]	20[a]	45[a]	70[a]
350–420 °C distillate lube oil							
1	Gas oil	220–295	250–303	214–285	9.54	4.80	5.86
2	Naphthenoparaffins	295–329	303–353	285–394	47.6	65.1	83.2
3	Mono/bi/polycyclic aromatics	329–468	353–452	394–504	28.4	22.6	6.23
4	Lacquer resins	468–511	452–484	504–555	14.5	7.53	4.70
420–500 °C distillate lube oil							
1	Gas oil	190–303	200–301	225–302	10.3	5.33	3.40
2	Naphthenoparaffins	303–353	301–403	302–406	40.0	56.12	78.1
3	Mono/bi/polycyclic aromatics	353–463	403–498	406–535	19.0	16.13	12.3
4	Lacquer resins	463–516	498–573	535–567	30.7	22.42	6.20
Residual base oil							
1	Gas oil	190–307	250–309	230–304	6.60	4.12	4.26
2	Naphthenoparaffins	307–394	309–430	304–467	45	58.25	64.2
3	Mono/bi/polycyclic aromatics	394–463	430–494	467–506	13.15	10.24	7.13
4	Lacquer resins	463–535	494–580	506–562	35.26	27.40	24.38

[a] Heating rates (°C/min).

In the table temperatures T_{st} (start) and T_{end} (end) are given for each fraction (sub-peak) in the column headed by the sample mass. These are the temperatures of the points on the DSC curve from which exponents separating the fractions from one another are drawn. In the last three columns relative heats α_1, α_2, and α_3 for each consecutive fraction (sub-peak) for samples of masses M_1, M_2, and M_3 are given. The relative heats giving relative weights of fractions in the mixture are calculated via formula

$$\alpha = \frac{\Delta H_{fr}}{\Delta H_t} \times 100\%,$$

where ΔH_{fr} is the oxidation heat of a fraction and ΔH_t is the total oxidation heat of all four fractions.

Comparison of curves in Figs. 1 and 2 and data of Table 2 show that increasing the sample mass from 3.2 to 14.6 mg has drastically changed the shape of the overall peak and temperatures of sub-peaks, as well as relative heats of each fraction for the light distillate lube oil. Instead of four well-defined sub-peaks of Fig. 1 one sees practically one broad peak in Fig. 2. The following regularities can be noted:

(i) The light fraction 1 (gas oil) is seen no more on the curve: its relative heat has dropped from $\alpha_1 = 13.8$ to $\alpha_3 = 0.27\%$;
(ii) The relative heat (relative weight) of fraction 2 (naphthenic) has increased from $\alpha_1 = 31.1$ to $\alpha_3 = 83.4\%$ and its T_{end} from 354 to 374 °C;
(iii) Fraction 4 (lacquer resin), in contrast, has gone down from $\alpha_1 = 27.8$ to $\alpha_3 = 2.4\%$. Its $T_{st} - T_{end}$ has decreased from 468–531 to 455–503 °C.

Regularity (i) can be explained by the increased diffusion resistance (due to thicker sample layer) for the light fraction whose release from the mixture is thereby shifted to higher temperatures where it is oxidized together with fraction 2. Its presence in fraction 2 lowers its T_{st} by several degrees.

Regularities (ii) and (iii) can be explained on the assumption that lacquer resins are formed from the naphthenic fraction of the sample during its oxidation. Lacquers are mainly formed on the metal surface and oxygen is essential for this process. If there is competition for oxygen between reactions in the bulk of the sample giving gaseous and low molecular weight condensation products, and those on the crucible surface giving high polymer resins (lacquers), than the thinner is the sample the greater portion of it is converted to lacquer resins. Their molecular weight and thus thermal stability is the greater the thinner is the sample layer (compare $T_{st} - T_{end}$ for samples 1 and 3, regularity (iii).

Thus, at least three reaction types can be assumed to occur in the temperature interval of oxidation of fraction 2: the one on the liquid sample surface where oxygen is plentiful and gaseous cracking products of low molecular weight are formed; the one in the bulk of the sample where low molecular weight condensation products are formed and later destroyed at some higher temperature, raising the T_{end} temperature of fraction 2 and producing or increasing fraction 3; and the one on the metal surface of the crucible giving rise to long-chain hard resins (lacquers) oxidizing at temperatures higher than 450 °C. The relative proportion of all these reactions depends on the sample initial chemical composition and on the conditions of the experiment, e.g. sample mass and heating rate.

The role of the sample composition can be seen from Table 2: the more heavy, more aromatic is the base oil, the higher are the temperatures of oxidation of its fractions. The regularities (i)–(iii) noted for the light base oil are valid for the other two base oils with the exception that for them the relative oxidation heat of fraction 4 does not fall below 14.5% and that of fraction 2 does not go beyond 61% on increasing the sample mass from 3.2 mg to 15–16 mg. This may be due to a greater content of high-boiling aromatics in the heavy oils—precursors of hard resins, which inevitably convert to the latter during heating at some temperature below their final destruction. Their molecular

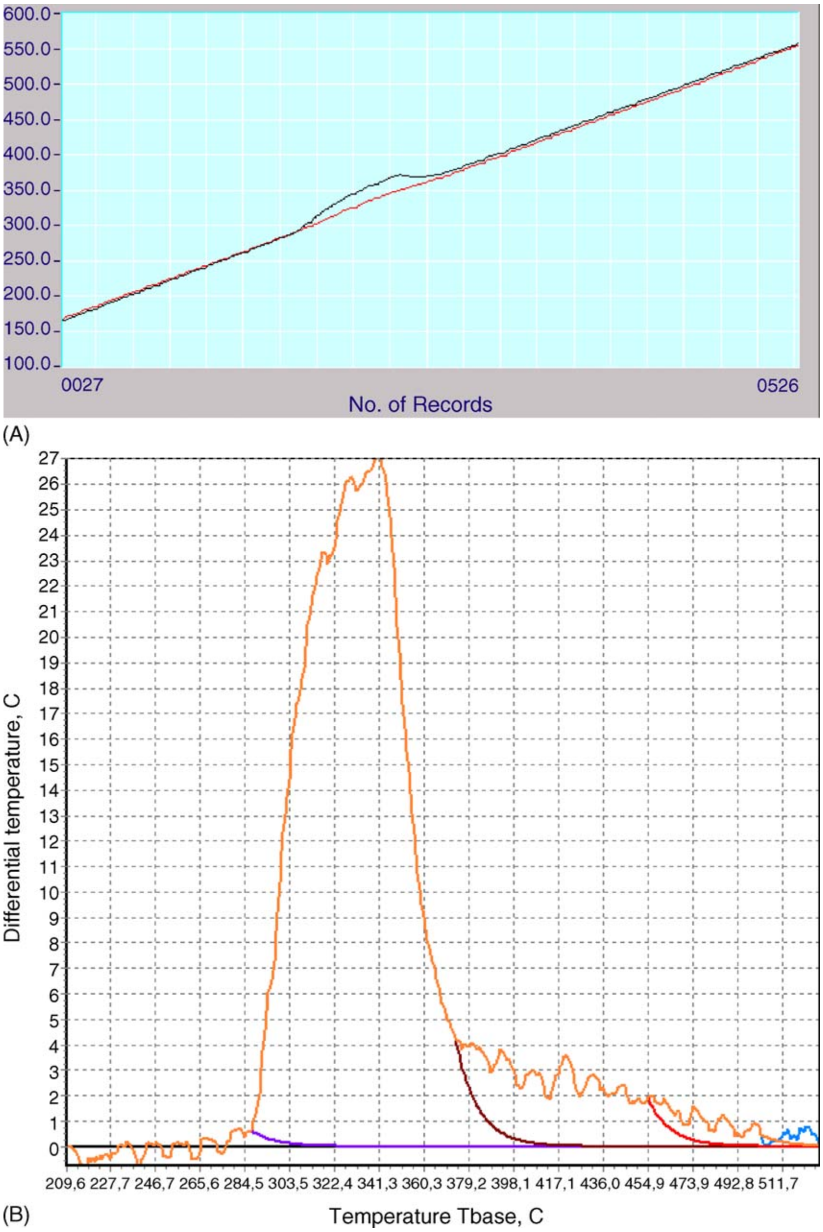

Fig. 2. DSC curves of light distillate base oil, $M = 0.0146$ g, $V = 45\,^{\circ}$C/min; (A) screen copy, (B) view in Deconvolution module of program Thermo.

weights as evidenced by the temperatures of oxidation are much higher than in the light oil, compare $T_{\mathrm{st}} - T_{\mathrm{end}}$ of fraction 4 of the light and the heavy base oils.

Now let us turn to the heating rate—the other major experimental factor of MDM. In Table 3, results similar to those of Table 2 are summed up for samples with masses 11–12 mg and heating rates 20, 45, and 70 °C/min, and in Fig. 3 the DSC curves dependence on the heating rate is illustrated for the middle base oil 420–500 °C.

It can be seen from the data presented that increasing heating rates from 20 to 45 to 70 °C/min acts very much like increasing sample masses: T_{st} of fraction 1 is shifted from 190 to 200 to 225 °C and α from 10.3 to 5.33 to 3.4 for the middle distillate base oil, showing that the light gas oil fraction does not have enough time to distill at low temperatures at high heating rates, and increasing portions of it join fraction 2 diluting it and lowering thereby its T_{st}. The latter effect is less pronounced for the heavy residual oil as it contains less gas oil.

In like manner, T_{end} of fraction 2 is raised sharply for all the three lube oils (by 40–70 °C) leading to a considerable broadening of the naphthenoparaffinic peak and simultaneous reduction of all the other peaks on the DSC curve, see Fig. 3.

High heating rates act similarly to large sample masses for the same reason that both high heating rates and large sample masses hinder fractions leaving the mixture at low temperatures. As a result, the oxidation reactions of all the fractions occur at higher temperatures changing their mechanism and giving products different from those obtained at lower heating rates or sample masses.

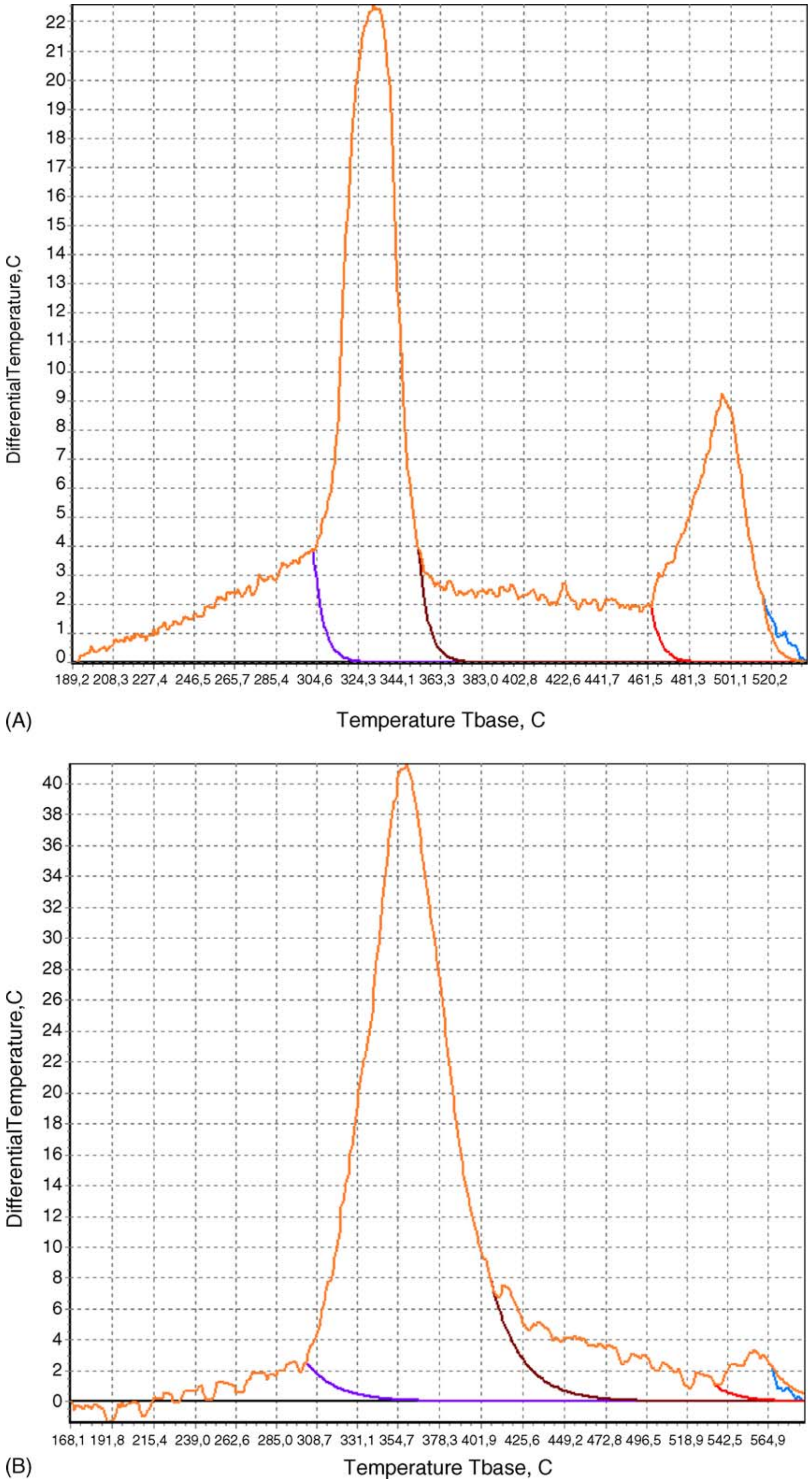

Fig. 3. DSC curves of middle distillate lube oil 420–500 °C, $m = 11$ mg. (A): $V = 20$ °C/min; (B): $V = 70$ °C/min.

Reactions giving lacquer resins are exothermic and thus run easier at low temperatures; they are slow and thus are favored by low heating rates; they require a metal surface on which they can form a stable polymeric film, and they require oxygen to generate enough reactive free radicals capable of initiating and maintaining long reaction chains. All these conditions are realized best when small samples, forming thin layers, and low heating rates are used.

Conversely, thick sample layers hinder the penetration of oxygen to the metal surface, while high heating rates bring the reaction into the high temperature region where quick oxidative cracking reactions are favored and low molecular species are mainly formed. In this way the fullness of oxidation is achieved, and the uncertainty of the obtained DSC results reduced, as less products not initially present in the sample are formed during the run (the presence of such products renders difficult the assessment of the initial fraction distribution in the lube oil). But this is achieved at the cost of reduced fraction resolution ability of the method, as the majority of HC fractions, and especially the lighter ones, are now crowded together at a higher temperature reaction region and combined in one broad peak, see Figs. 1–3.

One might now ask: what are the optimal conditions of the DSC experiment? The answer to this question depends on what is its aim, what are the tasks to be solved. If the aim is to assess the lacquer forming ability of the lube oil, i.e. its stability to oxidation, then small sample masses, say 3–5 mg, and low heating rates, say 20 deg/min, should be recommended. Large peaks above 450 °C will indicate a low oxidative stability of the lube oil. In this mode of operation, in addition, the light fraction content and its volatility can be determined best.

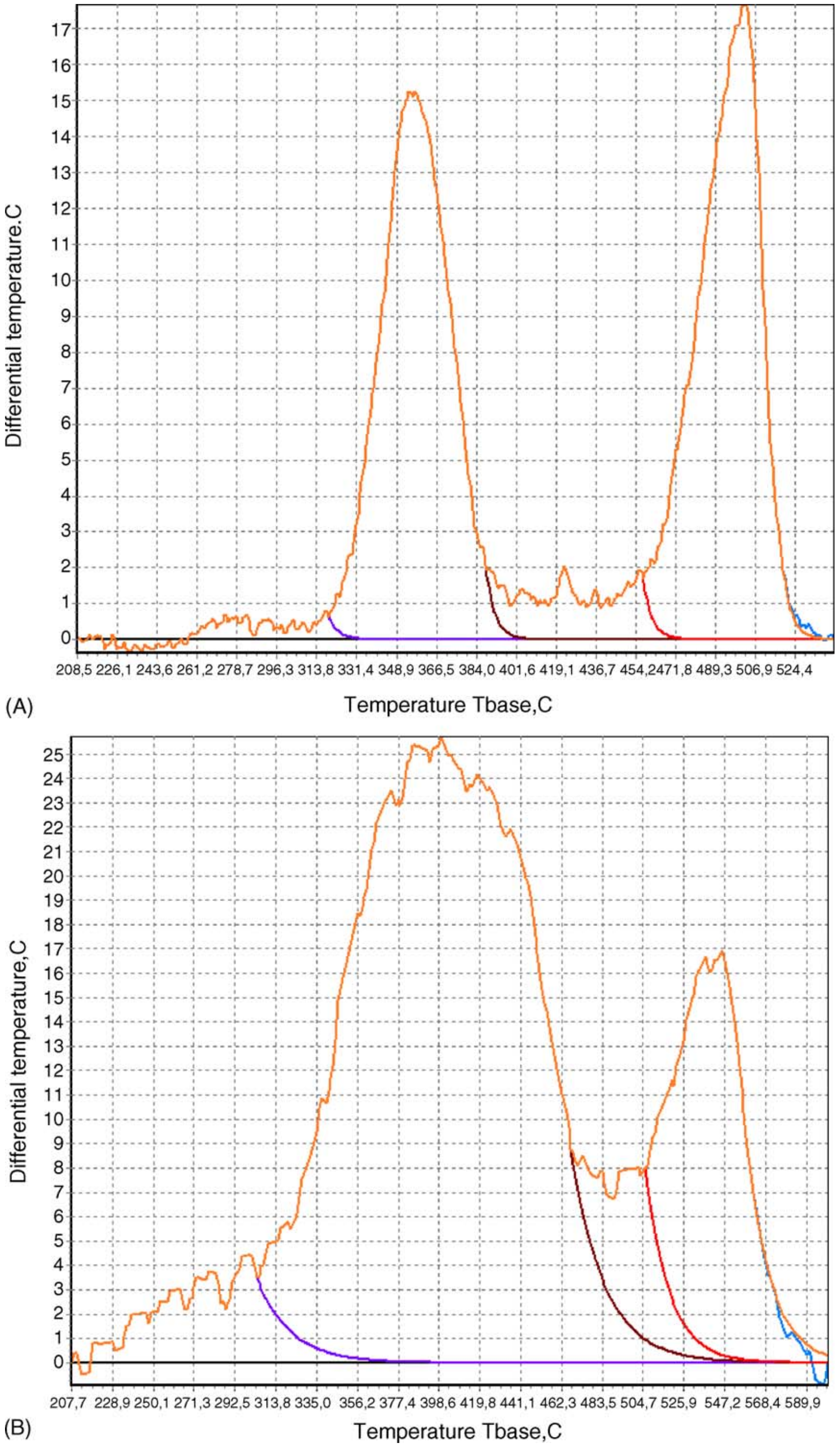

Fig. 4. DSC curves of residual base oil obtained at: (A) heating rate $V = 20\,^{\circ}$C/min, sample mass $M = 6.2$ mg; (B) $V = 70\,^{\circ}$C/min, $M = 12$ mg.
]

Table 4
Dependence of temperatures and relative oxidation heats of residual lube oil fractions (sub-peaks) on heating rates and sample masses

Number	Fraction	Sub-peak temperatures $T_{st} - T_{end}$ (°C)			Relative oxidation heats		
		20[a]	45[a]	70[a]	20[a]	45[a]	70[a]
$M = 0.0062$ g							
1	Gas oil	254–318	236–307	245–302	1.17	2.32	2.10
2	Naphthenoparaffins	318–388	307–425	302–439	35.34	42.53	51.91
3	Mono/bi/polycyclic aromatics	388–457	425–490	439–498	7.10	8.22	8.01
4	Lacquer resins	457–519	490–554	498–563	56.4	46.93	38.0
$M = 0.0120$ g							
1	Gas oil	197–307	260–309	207–304	6.60	2.12	4.26
2	Naphthenoparaffins	307–394	309–430	304–467	45.0	58.2	64.2
3	Mono/bi/polycyclic aromatics	394–464	430–495	467–506	13.15	10.24	7.13
4	Lacquer resins	464–535	495–580	506–562	35.26	29.42	24.4

[a] Heating rates (°C/min).

On the contrary, if one seeks to suppress the formation of species not initially present in the sample, and thus more fully assess the intrinsic naphthenoparaffinic content of the material and its molecular weight distribution, high heating rates (45–70 °C/min) and sample masses 12–15 mg should be used. This measure is more effective with respect to light and middle distillate lube oils than to heavy residual ones because the latter contain more high-boiling aromatic compounds easily (inevitably?) converted to hard resins under conditions of the DSC experiment. They may also contain hard resins as natural constituents, but to what extent remains unclear at this stage of investigation.

Thus, residual lube oils are a special case deserving a closer study. Samples with masses 6.2 and 12.0 mg were heated at rates from 20 to70 °C/min in order to find out the conditions of maximal and minimal hard resin formation (Table 4). In agreement with the regularities of thermal behavior of the lighter lube oils noted previously, the highest values of $M = 12.0$ mg and $V = 45$ and 70 °C/min gave the lowest hard resin content (relative oxidation heats 29.4 and 24.4%, respectively). Conversely, the lowest heating rate 20 °C/min and sample mass 6.2 mg gave the greatest value of this factor (56.4%). The DSC curves in Fig. 4 illustrate this feature of the residual lube oil thermal behavior in graphic form. It is seen that neither high heating rates nor large sample masses could help eliminate the formation of hard resins during the DSC run, presuming there are no intrinsic hard resins in the sample. But if there are such, then the final low value $\alpha = 24.4\%$ may characterize their initial (intrinsic) relative content in the sample, and the quantity $\Delta\alpha = 56.4 - 24.4 = 30\%$ would then show the ability of the lube oil to form hard resins under the given conditions of DSC experiment (Table 4).

4. Conclusions

(1) Some theoretical aspects of the method of dynamic microdistillation have been elaborated and experimentally validated using light and middle distillate and heavy residual lube base oils as model systems. In all cases, DSC curves exhibit two exothermic effects (peaks), the low-temperature one corresponding to oxidative distillation (cracking) of naphthenoparaffinic fraction, and the high-temperature one relating to oxidation of hard (packed) lacquer resins. The two heat effects (areas of the DSC peaks) are in inverse proportion to each other, indicating that lacquer resins are formed from the naphthenoparaffinic fraction of the sample.

(2) To study the intrinsic fraction distribution of the oil sample the extent of the lacquer forming reaction should be reduced and the extent of the gas producing cracking reaction enhanced. This is achieved by choosing higher heating rates and greater sample masses. The optimal values in this respect for the present method were found to be $V = 45–70$ °C/min and $M = 12–15$ mg.

(3) To study the oxidative stability of the oil, the lacquer forming reaction should be made predominant. This is achieved by choosing low heating rates, say 20 °C/min, and small sample masses on the order $M = 3–6$ mg (for the present method).

References

[1] B. Kowalski, Thermochim. Acta 250 (1995) 55.
[2] J.M. Perez, Thermochim. Acta 357–358 (2000) 47.
[3] O. Karacan, M.V. Kok, U. Karaaslan, J. Thermal Anal. Calorimetry 55 (1999) 109.
[4] D.W. Murray, et al., SAE SP 526 (1982).
[5] M. Ranjbar, G. Push, J. Appl. Pyrolysis 20 (1991) 185.
[6] M.V. Kok, O. Karacan, R. Pamir, Energy Fuels 12 (3) (1998) 580.
[7] O. Karacan, M.V. Kok, Energy Fuels 11 (2) (1997) 358.
[8] Yu.L. Shishkin, Thermochim. Acta 440 (2) (2006) 156.
[9] Yu.L. Shishkin, Thermochim. Acta 441 (2) (2006) 162.
[10] J.G. Speight, The Chemistry and Technology of Petroleum, second ed., Marcel Dekker Inc., New York, 1991.
[11] Yu.L. Shishkin, J. Thermal Anal. 29 (1984) 105.
[12] Yu.L. Shishkin, J. Thermal Anal. 32 (1987) 17.