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EVALUATION OF LOW-TEMPERATURE PROPERTIES OF GAS OILS VIA DIFFERENTIAL THERMAL ANALYSIS

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Gas oils with different wax contents were tested via a developed differential thermal analysis (DTA) procedure and also according to standard test methods. From the DTA curves, the following parameters were measured: onset peak temperature, maximum peak temperature and peak area. The variations of these DTA parameters with the standard properties for the gas oils, e.g. cloud, pour and cold filter plugging points and wax contents, were examined and were found to give linear relationships. Correlation coefficients between these results were calculated according to the established equations, which were also used for prediction of the standard properties for other gas oil samples from their DTA curves.

The precision limits for the developed DTA procedure were found to be satisfactory.

Those qualities which are related to the low-temperature performance of gas oils are of interest to both the petroleum fuel supplier and the consumer, and hence to the petroleum products researcher. These qualities arise as a result of the formation of wax crystals in gas oils due to temperature lowering, causing the plugging of fine filters and screens, the inability of vehicle pumps to pump the semi-solid fuel, or even the blocking of fuel lines [1].

The waxy hydrocarbon constituents that crystallize on cooling are, like all petroleum waxes, paraffinic in nature. The nature of the wax, however, depends on the type of paraffins present [2]. Normal-paraffins produce "macro" crystals. Noel [3] reported that DTA studies revealed two peaks when waxes were cooled. The higher-temperature peak was ascribed to wax crystallization and the lower-temperature peak to a solid-state transition [3]. On the other hand, iso-paraffins give rise to "micro" crystals, that yield only one endothermic effect, wax crystallization. Holder and Winkler [4] proved that the temperature of wax crystallization depends on the amount of wax and on the nature of the wax structure, i.e. not only the paraffinicity of the gas oil, but also on the nature of the

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crude from which it was produced. They also showed that only 2% of precipitated wax is required to gel the gas oil.

The low-temperature properties of gas oils are usually measured and evaluated through standard test methods. DTA has also been used to evaluate these properties [3–6]. DTA has many advantages over these standard methods, as it is faster, more precise and more sensitive.

In the present work, the development of a simple and precise DTA procedure has been considered for evaluation of the low-temperature properties of gas oils. The DTA parameters: onset peak temperature, maximum peak temperature and peak area are assumed to correlate with the standard low-temperature properties, i.e. the cloud point [7], pour point [8], cold filter plugging point [9] and wax content [10].

Experimental

Nine gas oil samples with different wax contents were analysed by the standard test methods [7–10] for their cloud point, pour point, cold filter plugging point and wax content, and the results are listed in Table 1. These samples were then analysed on a differential thermal analyser, which is sensitive for the evaluation of thermal behaviour over the temperature range +500 to −150°.

Table 1 Low-temperature properties of tested gas oil samples

Sample. No	Wax content, % wt.	Cloud point, °C	Pour point, °C	CFPP, °C
1	2.15	18	−3	12
2	3.22	18	0	14
3	4.3	21	15	17
4	5.37	24	15	18
5	6.45	24	18	21
6	7.52	27	21	23
7	8.6	30	24	24
8	9.67	33	27	30
9	10.75	33	27	33

The DTA procedure adopted was to take a pre-determined sample weight in the sample pan and place it in the head assembly, where a reference pan containing alumina was also placed. The head assembly was then heated to +46° as in the standard routine test methods. Afterwards, cooling with the aid of liquid nitrogen was started at a selected controlled rate and was continued to −15°. Meanwhile, the recorder displayed the thermal changes occurring in the sample, producing the corresponding DTA curve, from which the onset peak temperatures, maximum peak temperatures and peak areas were measured and used to evaluate the low-temperature properties of the tested samples.

The shape of a DTA curve depends on instrumental and operational parameters, as well as on the nature of the sample [3–5]. Accordingly, the effects of the operating parameters were studied and the following conditions, giving the best resolution, peak shape, etc. ..., were adopted:

sample weight: 20 mg; atmosphere: static air; programme: heat from ambient to +46°, hold for 5 minutes, cool to −15°; heating rate: 5 deg/min; cooling rate: 1 deg/min.

A microcomputer with a statistical application module was used to evaluate the degree of correlation between the DTA results, against those obtained from the standard test methods [7–10]. To evaluate the degree of confidence and magnitude of generalization for such correlations, five different gas oil samples were tested via both the DTA and the standard test methods. Calculated results for the cloud, pour and cold filter plugging points and the wax content from the DTA were compared with the actual measured results.

Results and discussion

When a waxy gas oil sample is cooled, crystallization occurs. This is an endothermic process and can be recorded as a characteristic peak in a DTA cooling curve. Figure 1 is a typical DTA curve for such a sample, with an endothermic peak and the shoulder of another endothermic process. The curve consists of the following parts:

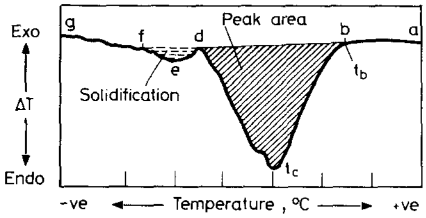

Fig. 1 A model for the DTA cooling curve

Part *ab* represents the initial cooling stage, i.e. before wax separation starts. The physical and chemical properties of the sample are nearly constant over this range, and consequently it is nearly horizontal. The temperature (t_b) corresponding to the point *b* is termed the onset temperature. It is related mainly to the wax crystallization temperature.

Peak *bcd* represents the endothermic energy change occurring due to the separation and crystallization of wax from the gas oil solution; t_c is the maximum peak temperature.

Shoulder *def* represents the solidification of the whole gas oil sample. In part *fg* the sample is in the solid state.

Figure 2 shows the difference between the DTA cooling curves of a wax-free gas oil sample and another with wax. The first sample was observed to give only a broad endothermic effect starting at a low temperature.

Figure 3 shows the DTA cooling curves for the tested samples. The effect of increasing wax content is observed as a shift in peak temperature and an increase in peak area for the wax crystallization endothermic peak. These peaks were observed to undergo slight splitting at higher wax contents. This splitting can be explained on the basis of the solid-state transition observed for "macro" wax crystals.

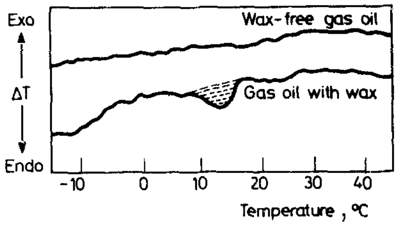

Fig. 2 DTA cooling curves of a wax-free gas oil and another with wax

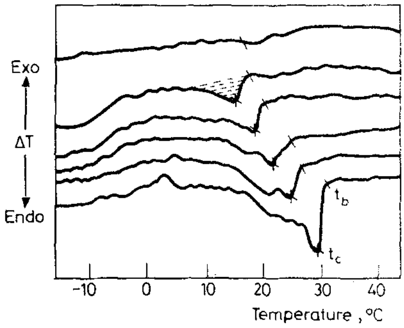

Fig. 3 DTA cooling curves of gas oil samples with different wax contents

Data from these curves, i.e. the onset peak temperatures, maximum peak temperatures and peak areas, are represented graphically against the cloud, pour and cold filter plugging points and the wax content in Figs 4, 6, 8 and 10, respectively.

Figure 4, which depicts the results for the three DTA parameters against the cloud points, shows a good correlation between these results. Such a correlation can be expressed by the following mathematical equations:

$$\text{Cloud point } (^\circ\text{C}) = 1.16\,S - 2.69\ldots \qquad (1)$$
$$R = 0.97$$

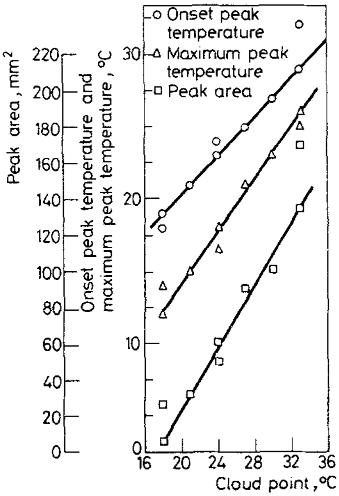

Fig. 4 Correlation between cloud points and DTA parameters (onset peak temperature, maximum peak temperature and peak area)

$$= 1.15\,P + 3.63\ldots \tag{2}$$

$$R = 0.99$$

$$= 0.08\,A + 17.14\ldots \tag{3}$$

$$R = 0.84$$

where:

S = onset peak temperature (°C);
P = maximum peak temperature (°C);
A = peak area (mm^2);
R = correlation coefficient.

The correlation coefficient (R) for each of the above equations indicates clearly that the cloud point is correlated well with these DTA parameters.

To evaluate the degree of confidence and the magnitude of generalization for Eqs 1–3, different gas oil samples were tested by both the DTA and the standard test method for the cloud point [7]. Values for cloud points as calculated from the DTA curves are presented graphically in Fig. 5 versus the actual measured values. From such a representation it is clear that there is good agreement between the calculated and measured cloud points, i.e. there is a possibility for the generalization of Eqs 1–3 for use with different gas oils. Accordingly, the cloud points can easily be predicted and calculated from the DTA curves by using any of the following DTA parameters: onset peak temperature, maximum peak temperature or peak area.

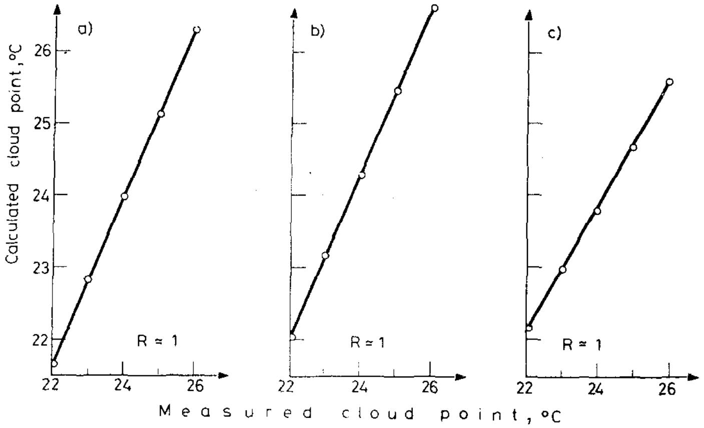

Fig. 5 Correlation between predicted and measured cloud points, based on: (a) onset peak temperature, C; (b) maximum peak temperature, °C; (c) peak area, mm^2

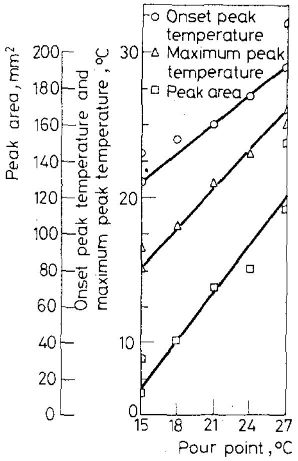

Fig. 6 Correlation between pour points and DTA parameters (onset peak temperature, maximum peak temperature and peak area)

Similarly, Fig. 6 shows the correlation between the pour points and the three DTA parameters for the tested samples. The correlation coefficient for each of the following equations indicates that the correlation is rather rough for the pour point results:

$$\text{Pour point } (^\circ\text{C}) = 2.02\, S - 32.81 \ldots \qquad (4)$$

$$R = 0.90$$

$$R = 1.99\,P - 21.71\ldots \qquad (5)$$
$$R = 0.92$$
$$= 0.18\,A - 0.67\ldots \qquad (6)$$
$$R = 0.87$$

These lower values for R may be due to the decrease in accuracy of the standard pour point test (± 6°) as compared to the cloud point (± 1°). This can be seen from the values for samples 3 and 4, where although they have the same pour points, the DTA results yield different values.

Again, the values obtained by calculation from the DTA parameters for the different gas oil samples are compared to the experimental values as seen in Fig. 7. There is relatively good agreement between the calculated and measured pour points.

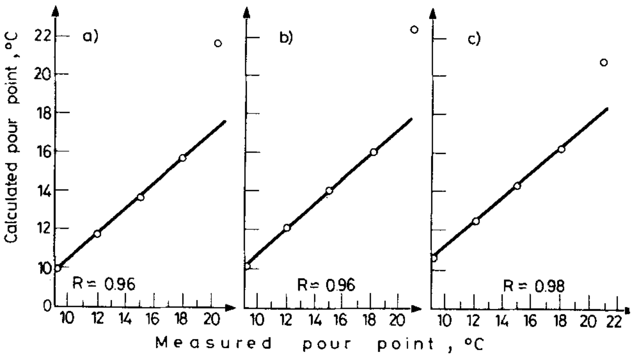

Fig. 7 Correlation between predicted and measured pour points, based on: (a) onset peak temperature, °C; (b) maximum peak temperature, °C; (c) peak area, mm^2

Figure 6 shows the correlation between the DTA parameters and the cold filter plugging points (CFPP). The following equations were obtained:

$$\text{Cold filter plugging point (°C)} = 1.43\,S - 13.21\ldots \qquad (7)$$
$$R = 0.99$$
$$= 1.36\,P - 4.49\ldots \qquad (8)$$
$$R = 0.98$$
$$= 0.13\,A + 9.22\ldots \qquad (9)$$
$$R = 0.99$$

The values in this case are observed to be well correlated. This may be due to the fact that the CFPP method is an automatic and fairly accurate technique.

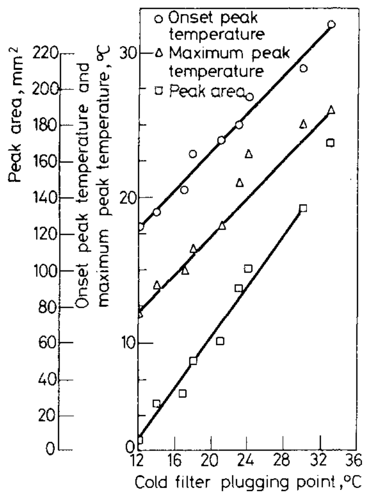

Fig. 8 Correlation between cold filter plugging and DTA parameters (onset peak temperature, maximum peak temperature and peak area)

Predicted results from the DTA curves and the experimental values for CFPP are illustrated graphically in Fig. 9, which shows the linearity between the two methods.

The variations in DTA parameters and wax content of the tested samples are illustrated in Fig. 10. In this case, only the DTA maximum peak temperatures and peak areas are plotted, since the onset peak temperature corresponds to the first

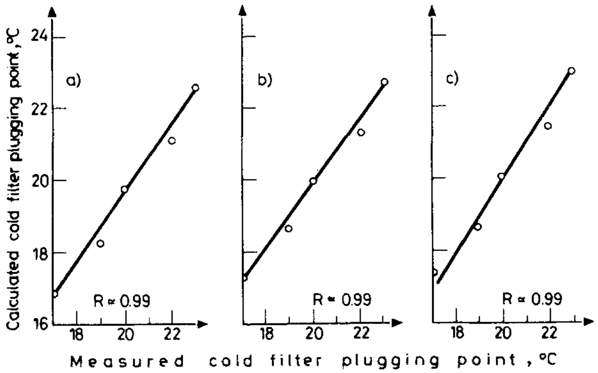

Fig. 9 Correlation between predicted and measured cold filter plugging points, based on: (a) onset peak temperature, °C; (b) maximum peak temperature, °C; (c) peak area, mm²

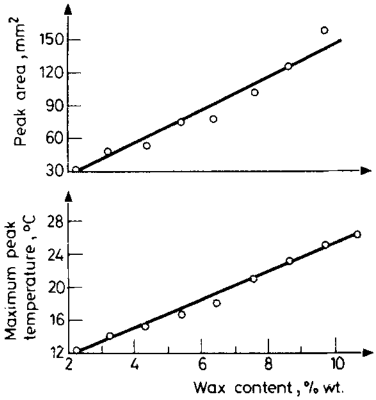

Fig. 10 Correlation between wax contents and DTA parameters (maximum peak temperature and peak area)

separation of wax crystals and not the separation of all the wax present. Hence, the following relations were obtained:

$$\text{Wax content (\% wt)} = 0.59\,P - 4.71\ldots \quad (10)$$

$$R = 0.99$$

$$= 0.05\,A + 1.21\ldots \quad (11)$$

$$R = 0.98$$

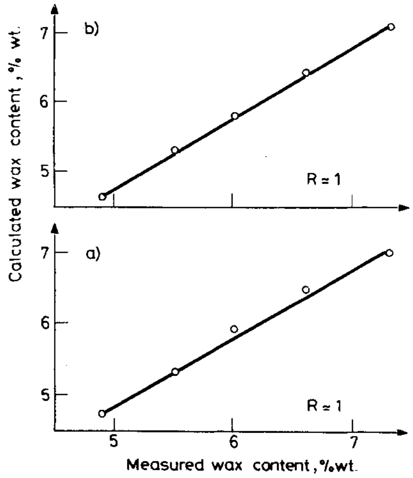

Fig. 11 Correlation between predicted and measured wax content based on: (a) maximum peak temperature, °C; (b) peak area, mm^2

Predicted results for the wax contents as calculated from the DTA parameters, and the actual wax contents for different gas oil samples are shown graphically in Fig. 11, where a linear relation over the tested wax content range is observed.

In general, the above relations (Eq. 1–11) indicate that the DTA method is a suitable technique for providing worthwhile information concerning the low-temperature properties of different gas oil samples.

The precision of this technique was examined by testing one sample several times under the same conditions and by the same operator. The data obtained were substituted into the standard deviation equation and the calculated limit was found to be ±0.78° for the onset peak temperature, ±0.83° for the maximum peak temperature, and within 2.9% of the mean value of two results for the peak area.

Conclusion

Differential thermal analysis (DTA) was adopted to evaluate the low-temperature properties of gas oils with different wax contents from ambient temperature to 46°, followed by cooling to $-15°$. The energy released in the crystallization temperature ranges was recorded in the resulting DTA curves. These curves showed a clear response to the changes in wax content of the tested samples. The peak temperatures (i.e. the onset and maximum peak temperatures) and areas of the DTA curves were compared with the wax contents and were found to be correlated ($R \simeq 0.98$–0.99). These DTA curves were also compared with the standard low-temperature properties of gas oils, namely the pour point, cloud point and cold filter plugging point. Correlation coefficients for peak temperatures and areas versus these standard properties were calculated ($R \simeq 0.92$–0.99). Results for the standard properties as calculated from the DTA curves were found to be in good agreement with the actual measured results. This new DTA procedure can be recommended as a precise, simple and fast quality control method for gas oils.

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Zusammenfassung — Dieselöle mit unterschiedlichem Wachsgehalt wurden nach einem neu entwickelten DTA-Verfahren und auch nach Standardmethoden getestet. Folgende Parameter Wurden aus den DTA-Kurven bestimmt: die Temperaturen zu Beginn und beim Maximum des Peakes und die Peakfläche. Zwischen Veränderungen dieser DTA-Parameter und den Standardeigenschaften der Dieselöle, wie z. B. Trübungs-, Fließ- und Kaltfilterverstopfungspunkt sowie Wachsgehalt, wurden lineare Zusammenhänge festgestellt. Korrelationskoeffizienten wurden nach den bekannten Gleichungen berechnet, die auch zur Vorhersage der Standardeigenschaften anderer Dieselöle aus DTA-Kurven herangezogen wurden. Die Genauigkeitsgrenzen der ausgearbeiteten DTA-Methode sind ausreichend.

Резюме — Дизельные топлива с различным содержанием вокса были исследованы усовершенствованным методом дифференциального термического анализа (ДТА), согласно стандартным тестовым методам. Из ДТА-кривых были измерены следующие параметры: начало температурного пика, максимум температурного пика и площадь пика. Исследовано изменение этих параметров в зависимости от таких стандартных характеристик дизельных топлив, как температуры помутнения, застывания, закупорки фильтра на холоду и содержанием воска и найдена для них линейная корреляция. Коэффициенты корреляции были вычислены согласно установленным уравнениям, которые были также использованы для определения стандартных параметров других образцов дизельного топлива на основе их ДТА-кривых. Пределы точности усовершенствованного метода ДТА найдены удовлетворительными.