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DETERMINATION OF CLOUD POINT FOR PETROLEUM MIDDLE DISTILLATES BY DIFFERENTIAL SCANNING CALORIMETRY

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SUMMARY

A method for determining the cloud point of petroleum middle distillates by differential scanning calorimeter (DSC) has been developed. None of the 95 samples failed to crystallize at a rapid cooling rate on the DSC, and the degree of supercooling was quite low. The onset temperature of the crystallization peak tended to be a few degrees lower than the cloud point measured by the standard method, ASTM D-2500, but a very good correlation between the onset temperature of the crystallization peak and cloud point was found. On the basis of this correlation the cloud point can be determined satisfactorily by DSC. The new method is over three times more accurate and two to eight times less time consuming than the standard ASTM method.

INTRODUCTION

Low temperature properties are very important in certain petroleum products, especially if these products are used in a cold climate such as in Finland and the other Nordic countries. The cloud point serves as an index of the lowest temperature at which e.g. diesel oils or light fuel oils, for example, can be used. Rapid and accurate determination of this property is important both for the final products and for controlling the refining process.

The cloud point is usually determined by ASTM method D 2500. This is, however, very time consuming and not highly accurate. Depending on the sample, a single determination takes between half an hour and two hours, and repeatability is 2 °C.

The literature contains some examples of determination of the cloud point by differential scanning calorimeter (DSC) in which the onset point of the crystallization peak is utilized. F. Noel (ref. 1) obtained a fairly good correlation between ASTM and DSC results with different kind of oil products. The temperature range is, however, very wide and it is not possible to assess the accuracy. In contrast, P. Redelius (ref. 2) did not manage to find a reasonable correlation for transformer and lubricating

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oils. F. Bosselet et al. (ref. 3) stated that the cloud points of gas oil can be determined satisfactorily with a repeatability of 0.4 °C. However, in this case only two different oil samples were examined.

The purpose of the present work was to find out if the cloud points of middle distillates could be determined by DSC with better precision and more rapidly than by the standard ASTM D 2500-81 method.

EXPERIMENTAL

Most of the 95 samples were gas oil and kerosene fractions from both straight runs and different kinds of cracking units. Some diesel oil samples (nos. 1 to 4) were also included.

The cloud points were determined using the standard ASTM D 2500-81 method. DSC measurements were carried out with a Mettler TA 3000, DSC 30. To obtain the crystallization peak, samples of weight 5 to 15 mg were cooled from +35 °C to 100 °C using a cooling rate of 10, 5 or 2 °C/min. The onset point was determined using the programme for oxidation stability in the equipment. Two different temperatures were given as shown in Fig. 1. The point where the curve deviates from the base line was called T1 and the point of intersection of the two regression lines was called T2. The threshold value was selected so that the tangent touched the deepest part of the curve.

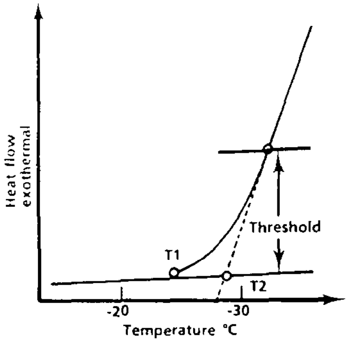

Fig. 1. Determination of the onset point. The first regression line follows the curve before the start of the peak. The second regression line is the tangent to the curve at the point which differs from the first regression line by a specified threshold value.

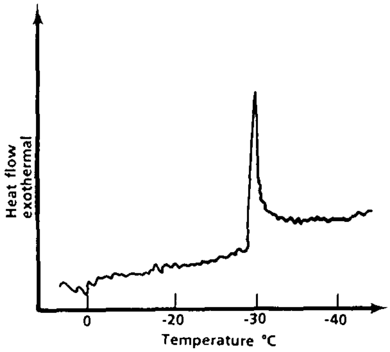

Fig. 2. A typical crystallization peak.

RESULTS AND DISCUSSION

The influence of the cooling rate

Thermodynamic barriers to crystal nucleation on cooling cause the liquid to supercool before the crystallization begins. However, once crystallization has started it proceeds rapidly, and at a few degrees below the onset of freezing the sample is close to equilibrium with respect to the fraction of solid frozen out. This accounts for the mode of the typical crystallization peak in Fig. 2. The amount of supercooling depends on the sample and of course on the cooling rate. In order to assess the latter effect, we made DSC runs for six samples using rates of 10, 5 and 2 °C/min. Results for T2 are presented in Table 1. The exact onset temperatures could be obtained for all the samples at 10 °C. At the lower cooling rates the beginning of the peak was so gradual that determination of the onset point was uncertain. On the other hand, lowering of the cooling rate from 10 °C to 2 °C/min changed T2 by less than 1 °C. Thus supercooling seems to be fairly low, even at the highest cooling rate of 10 °C/min. This rate was therefore chosen for the remainder of the samples.

TABLE 1

Temperatures T2 at different cooling rates (°C).

Sample No.	ASTM cloud point	T2		
		10 °C/min	5 °C/min	2 °C/min
1	- 2	- 6.3	- 5.7	- 5.5
2	-21	-20.7	~-21	-
3	-23	-24.5	~-23	~-22
4	-27	-28.9	-28.3	~-28
5	+ 8	+ 3.5	+ 4.0	+ 4.2
6	-27	-30.0	-29.9	-29.4

Onset points of the crystallization exotherm

Two parallel runs were made for each sample by DSC. The averages of the onset temperatures (T1 and T2) and the differences between the parallel determinations (d_{T1} and d_{T2}) together with the ASTM cloud points are listed in Table 2. The standard deviation can be calculated according to the following equation

$$s = \sqrt{d^2}/2n$$

where d is the difference between the parallel determinations and

TABLE 2
ASTM cloud points and DSC results (°C).

Sample no.	ASTM cloud point	DSC results							
		T1	d_{T1}	T2	d_{T2}	C1	ΔC1	C2	ΔC2
7	-37	-36.9	0.1	-37.2	0.2	-34.9	-2	-34.6	-2
8	-35	-35.5	0.3	-35.7	0.5	-33.5	-2	-33.0	-2
9	-35	-34.4	0.0	-34.7	0.2	-32.3	-3	-32.0	-3
10	-34	-35.0	0.3	-35.2	0.1	-33.0	-1	-32.5	-1
11	-33	-36.2	0.3	-36.6	0.1	-34.2	+1	-34.0	+1
12	-33	-33.5	0.1	-33.7	0.0	-31.4	-2	-30.9	-2
13	-32	-32.7	0.6	-33.2	0.2	-30.6	-1	-30.4	-2
14	-31	-30.4	0.0	-31.9	0.1	-28.3	-3	-29.1	-2
15	-30	-32.0	0.2	-32.8	0.1	-29.9	-0	-30.0	+0
16	-30	-32.3	0.6	-32.4	0.5	-30.2	+0	-29.6	-0
17	-30	-30.8	0.3	-31.9	0.0	-28.7	-1	-29.1	-1
18	-29	-30.3	0.9	-31.3	0.0	-28.2	-1	-28.4	-1
19	-29	-30.7	0.3	-32.3	0.3	-28.6	-0	-29.5	+0
20	-29	-31.1	0.3	-32.2	0.0	-29.0	-0	-29.4	+0
21	-29	-30.5	0.4	-31.3	0.1	-28.4	-1	-28.4	-1
22	-29	-30.3	0.3	-30.7	0.2	-28.2	-1	-27.8	-1
23	-29	-31.0	0.1	-32.5	0.0	-28.9	-0	-29.7	+1
24	-29	-30.9	0.2	-31.8	0.4	-28.8	-0	-29.0	-0
25	-29	-29.3	0.0	-29.8	0.1	-27.1	-2	-26.9	-2
26	-29	-31.3	0.0	-31.8	0.0	-29.2	+0	-29.0	-0
27	-29	-30.7	0.4	-31.2	0.5	-28.6	-0	-28.3	-1
28	-28	-31.3	0.3	-32.0	0.5	-29.2	+1	-29.2	+1
29	-28	-30.9	0.4	-32.0	0.2	-28.8	+1	-29.2	+1
30	-28	-31.1	0.1	-31.6	0.4	-29.0	+1	-28.8	+1
31	-28	-29.2	0.0	-30.4	0.3	-27.0	-1	-27.5	-1
32	-28	-31.1	0.4	-31.8	0.3	-29.0	+1	-29.0	+1
33	-28	-30.5	0.2	-31.5	0.1	-28.4	+0	-28.6	+1
34	-28	-28.9	0.0	-29.7	0.0	-26.7	-1	-26.8	-1
35	-28	-29.5	0.1	-29.8	0.0	-27.3	-1	-26.9	-1
36	-27	-28.2	0.1	-29.4	0.2	-26.0	-1	-26.4	-1
37	-27	-29.6	0.1	-30.4	0.1	-27.4	+0	-27.5	+0
38	-27	-29.3	0.1	-30.0	0.2	-27.1	+0	-27.1	+0
39	-27	-30.5	0.5	-31.2	0.5	-28.4	+1	-28.3	+1
40	-27	-30.0	0.5	-30.1	0.7	-27.9	+1	-27.2	+0
41	-27	-30.5	0.0	-31.1	0.2	-28.4	+1	-28.2	+1
42	-27	-31.3	0.2	-31.6	0.2	-29.2	+2	-28.8	+2
43	-27	-30.0	0.0	-30.8	0.1	-27.9	+1	-27.9	+1
44	-27	-30.7	0.4	-31.2	0.4	-28.6	+2	-28.3	+1
45	-27	-28.9	0.1	-30.4	0.0	-26.7	-0	-27.5	+0
46	-27	-30.2	0.1	-30.8	0.2	-28.1	+1	-27.9	+1
47	-26	-28.1	0.1	-29.2	0.1	-25.9	-0	-26.2	+0
48	-26	-29.6	0.1	-30.9	0.4	-26.4	+0	-28.0	+2
49	-26	-29.4	0.0	-30.2	0.0	-27.4	+1	-27.3	+1
50	-26	-28.6	0.1	-29.5	0.5	-27.2	+1	-26.6	+1
51	-25	-29.9	0.2	-30.4	0.3	-27.8	+3	-27.5	+2
52	-25	-28.3	0.5	-28.8	0.6	-26.1	+1	-25.8	+1
53	-25	-29.0	0.0	-29.4	0.1	-26.8	+2	-26.4	+1
54	+ 1	- 0.4	0.1	- 1.8	0.2	+ 2.4	-1	+ 2.4	-1
55	+ 1	- 0.1	0.4	- 2.3	0.1	+ 2.7	-2	+ 1.9	-1
56	+ 1	- 0.2	0.7	- 1.7	0.3	+ 2.6	-2	+ 2.5	-2
57	+ 2	- 0.6	0.0	- 2.4	0.1	+ 2.2	-0	+ 1.8	+0
58	+ 2	- 1.1	0.1	- 2.2	0.0	+ 1.6	+0	+ 2.0	-0
59	+ 2	- 2.7	1.7	- 1.6	1.2	+ 0.0	+2	+ 2.6	-1
60	+ 2	+ 0.1	0.1	- 1.7	0.3	+ 2.9	-1	+ 2.5	-1
61	+ 2	- 1.2	0.3	- 2.4	0.4	+ 1.5	+0	+ 1.8	+0
62	+ 2	+ 0.0	0.0	- 1.7	0.5	+ 2.8	-1	+ 2.5	-1
63	+ 2	+ 0.4	0.7	- 1.1	0.2	+ 3.2	-1	+ 3.2	-1
64	+ 2	- 0.9	0.5	- 2.5	0.0	+ 1.9	+0	+ 1.7	+0
65	+ 2	+ 0.3	0.3	- 0.4	0.2	+ 3.1	-1	+ 3.9	-2
66	+ 3	+ 0.7	0.1	- 1.0	0.4	+ 3.5	-0	+ 3.3	-0
67	+ 3	- 0.6	0.1	- 1.6	0.1	+ 2.2	+1	+ 2.6	+0
68	+ 3	- 0.4	1.3	- 1.6	0.0	+ 2.4	+1	+ 2.6	+0
69	+ 3	+ 0.7	0.0	- 0.9	0.1	+ 3.5	-0	+ 3.4	-0
70	+ 3	+ 1.4	0.9	- 0.5	0.6	+ 4.2	-1	+ 3.8	-1
71	+ 3	+ 0.8	0.5	- 0.9	0.4	+ 3.6	-1	+ 3.4	-0
72	+ 3	+ 0.8	0.2	- 0.4	0.1	+ 3.6	-1	+ 3.9	-1
73	+ 3	+ 0.6	0.7	- 1.2	0.4	+ 3.4	-0	+ 3.1	-0
74	+ 3	+ 0.4	0.1	- 0.8	0.2	+ 3.2	-0	+ 3.5	-0
75	+ 3	+ 0.4	0.2	- 1.8	0.5	+ 3.2	-0	+ 2.4	+1
76	+ 3	- 0.3	0.0	- 1.6	0.0	+ 2.5	+1	+ 2.6	+0
77	+ 3	+ 0.2	0.2	- 1.0	0.1	+ 3.0	+0	+ 3.3	-0
78	+ 3	- 0.2	0.3	- 1.7	0.3	+ 2.6	+0	+ 2.5	+0
79	+ 3	- 0.6	0.9	- 2.5	0.2	+ 2.2	+1	+ 1.7	+1
80	+ 3	- 0.5	0.3	- 2.7	0.2	+ 2.3	+1	+ 1.5	+2
81	+ 4	+ 0.5	0.1	- 1.6	0.4	+ 3.3	+1	+ 2.6	+1
82	+ 4	+ 1.8	1.0	+ 0.1	0.3	+ 4.6	-1	+ 4.4	-0
83	+ 4	+ 1.1	0.3	+ 0.1	0.1	+ 3.9	+0	+ 4.4	-0
84	+ 4	+ 0.3	0.0	- 1.7	0.0	+ 3.1	+1	+ 2.5	+1
85	+ 5	+ 1.2	0.2	+ 0.1	0.2	+ 4.0	+1	+ 4.4	+1
86	+ 5	+ 3.4	0.5	+ 1.8	0.5	+ 6.2	-1	+ 6.2	-1
87	+ 5	+ 1.8	0.1	+ 0.1	0.2	+ 4.6	+0	+ 4.4	+1
88	+ 5	+ 1.3	0.2	- 0.7	0.2	+ 4.1	+1	+ 3.6	+1
89	+ 5	+ 2.5	0.1	+ 0.5	0.0	+ 5.3	-0	+ 4.8	+0
90	+ 6	+ 2.6	0.5	+ 1.9	0.4	+ 5.4	+1	+ 6.3	-0
91	+ 7	+ 2.6	0.5	+ 1.3	0.5	+ 5.4	+2	+ 5.7	+1
92	+ 7	+ 4.0	0.3	+ 1.4	0.4	+ 6.9	+0	+ 5.8	+1
93	+ 8	+ 2.8	0.3	+ 2.0	0.3	+ 5.6	+2	+ 6.4	+2
94	+ 8	+ 5.3	0.2	+ 2.9	0.2	+ 8.2	-0	+ 7.3	+1
95	+19	+17.0	0.0	+16.0	1.0	+20.1	-1	+21.0	-2

n is the number of samples. The standard deviations s_{T1} and s_{T2} are 0.247 and 0.204, respectively.

Correlation of T1 and T2 with the ASTM cloud points

Temperatures T1 and T2 tend to be respectively 2.8 °C and 4.3 °C lower, on average, than the ASTM cloud points. At the time this article was written, P. Claudy et al. presented similar results for diesel oils (ref. 4). The difference between the onset temperature and the ASTM cloud point in their work was also about -3 °C to -4 °C despite the low cooling rate (0.5 °C/min). This is consistent with my observation that the cooling rate has little effect on the results. According to P. Claudy et al. the systematic deviation in question can be explained by the thermal gradient for the sample during cooling. In the ASTM apparatus, the sample temperature is measured at the centre of the test tube and the precipitated paraffins appear on the colder walls of the tube.

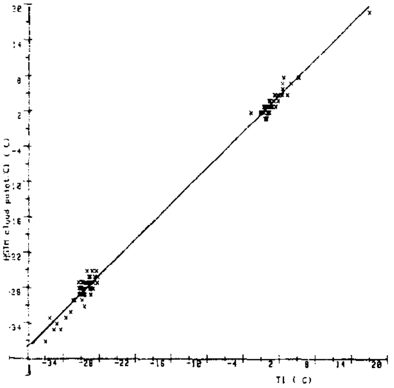

Fig. 3. Correlation of the ASTM cloud point and T1

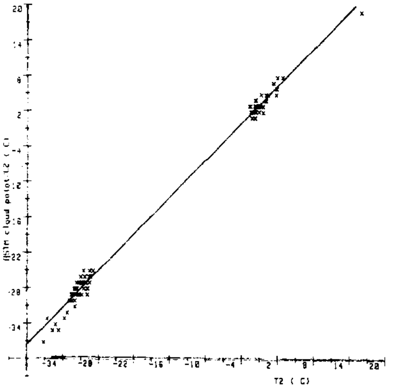

Fig. 4. Correlation of the ASTM cloud point and T2

Correlations are good, however, between onset temperatures T1 and T2 and the ASTM cloud points, as shown in Figs 3 and 4. The equations of the regression lines are as follows

$$C1 = 1.021\ T1 + 2.77 \qquad (2)$$

$$C2 = 1.046\ T2 + 4.31 \qquad (3)$$

with the correlation factors being 0.9977 and 0.9976, respectively. The values of C1 and C2 calculated according to equations (2) and (3) correspond to the ASTM cloud points and we refer to them as DSC cloud points.

In order to assess more accurately the suitability of DSC measurements for determining cloud points, we calculated C1 and C2 according to the above equations. The results are in Table 2 together with their differences from ASTM cloud points $\Delta C1$ and $\Delta C2$. In the whole series of 89 samples, the difference $|\Delta C1|$ is more than 2 °C in only three cases. The value of $|\Delta C2|$ is greater than 2 °C for only one sample. On the other hand, the repeatability of the ASTM method at a 95% probability level is 2 °C. The differences between the ASTM and DSC cloud points are not, therefore, significant.

Taking account of equations (2) and (3), we obtain the following standard deviations:

$s_{C1} = 1.021 \quad s_{T1} = 0.252$ and
$s_{C2} = 1.046 \quad s_{T2} = 0.213$

According to ASTM E 691-79, repeatabilities r_{C1} and r_{C2} on the 95% probability level can be calculated as follows:

$r_{C1} = 2\sqrt{2}\ s_{C1} = 0.71$ and
$r_{C2} = 2\sqrt{2}\ s_{C2} = 0.60$

So the repeatability of the temperatures' C2 is a little better than that of C1.

CONCLUSION

The cloud point of various greatly differing middle distillates can be determined satisfactorily by DSC using the onset temperature of the crystallization peak. One determination takes only 15 min and the repeatability is as good as 0.6 °C.

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