

MONITORING WAX CRYSTALLISATION IN DIESEL USING DIFFERENTIAL SCANNING CALORIMETRY (DSC) AND MICROCALORIMETRY

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Abstract

The crystallisation of wax on cooling a diesel was monitored by DSC with cooling rates of 5-0.2 °C/min and by a microcalorimeter with the lower rates of 0.1-0.01 °C/min. The melting of crystallised wax was also monitored by DSC to assess the thermodynamic reversibility of the process. The results show that crystallisation temperatures from DSC at a cooling rate of 1 °C/min are close to those from microcalorimetry at 0.01 °C/min (a realistic cooling rate for diesel in a vehicle). A comparison of crystallisation and melting data shows that equilibrium crystallisation conditions are not achieved even at the lowest cooling rate used here.

1. INTRODUCTION

When crudes, diesels or mineral lubricating oils are cooled, a temperature is reached at which the wax in the sample begins to crystallise. This temperature and the amount of wax which has crystallised when a specified temperature is reached are measured in various national standard methods. These methods use apparatus dedicated to the specific test and generally require large amounts of sample and laborious procedures.

DSC can detect the (exothermic) onset of wax crystallisation on cooling a diesel and can measure the amount of heat evolved, and the latter value can be converted to %wax as will be explained below. However, the main problem in applying DSC is the choice of the cooling rate. If too low, the test takes a long time; if too high, there is supercooling. Obviously there must be a compromise but there is little information on what it should be and what errors are likely.

Bosselet et al [1] have used DSC to monitor the crystallisation of wax from a diesel cooled at rates in the range 3.5-0.2 °C/min and found an approximately linear dependence of onset of crystallisation on the rate of cooling. They also considered the problem of calculating the %wax in a diesel from the integrated DSC curve. Here there are complications because the enthalpy of crystallisation of a wax in a diesel depends on the molar mass of the wax and the heat of solution of the wax in the diesel. However, they solved this problem by making several mixtures from wax-free diesel plus pure hydrocarbon waxes and related the DSC data to the known amounts of the waxes. The following relationship

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was derived, which relates the enthalpy of crystallisation in J/g to the Celsius temperature at which crystallisation is occurring:

$$\Delta H = 1.5167 T + 211.7 \quad (1)$$

In a later study, Claudy et al [2] studied a set of 40 diesels (without pour point depressants) with a cooling rate of 0.5 °C/min. Using various features of the DSC curves and areas, they derived correlations between DSC data and ASTM cloud and pour points, and European filter plugging point, noting that DSC was more precise and could obtain all these parameters from a single run. They followed this by a similar study [3] on crudes and their distillates, showing that DSC could measure %wax.

The above studies still leave unanswered the important question: how closely does a DSC wax crystallisation temperature obtained at low cooling rates (eg < 5 °C/min) approximate to real situations, where the cooling rate is much lower (eg 0.01 °C/min)?

This study attempts to answer this in two ways: (a) By using a microcalorimeter, which is in effect a DSC which can accommodate a large sample and therefore can produce measurable heat flowrate signals at cooling rates as low as 0.01 °C/min, where DSC signals would be obscured by noise. (b) By studying the melting of crystallised diesel.

Melting was studied because, in general, the amount of superheating during melting is much less than the amount of supercooling during crystallisation, so melting points are usually regarded as being a much better measure of the equilibrium solid-liquid coexistence temperature. For a diesel, ideally the onset of crystallisation will occur at the same temperature as the completion of melting if the cooling/heating rates are sufficiently low. As will be seen below, the disparity is surprisingly large.

This work was limited to a single diesel, with no pour point depressant, and it was chosen because it has a wax crystallisation temperature near 0 °C, a temperature at which water can be used for the calibration of both the DSC and the microcalorimeter. This was considered desirable because it guarantees that there will be no significant error in comparing measured temperatures from the two instruments.

2. DSC EXPERIMENTS

In addition to the standard calibration procedure, the Mettler DSC30 was further calibrated at a heating rate of 0.5 °C/min to give the correct melting points of double de-ionised water and high-purity mercury and the correct

melting enthalpy for double de-ionised water. The DSC30 control system compensates for the variation in thermal lags at different heating/cooling rates and thereby ensures that the true sample temperature is always recorded. Samples of mass 60 mg were sealed into 150 μ l aluminium pans, and 2 x 60 mg discs of sapphire were sealed into the reference pan; the purge gas was 100 ml/min dry N₂. Although the reference pan is usually empty for DSC, the 120 mg of sapphire was used to equalise the heat capacity of the sample and resulted in a much less noisy signal at the lower cooling rates.

For the crystallisation experiments, the sample was cooled from 30 °C to -5 °C at the desired rate (0.2-5.0 °C/min); for the melting experiments, the sample was first cooled from +30 °C to -30 °C at 5 °C/min, then heated at the chosen rate (0.2-1.0 °C/min).

The data was processed using the Mettler Graphware TA72.5 package. This allows the onset of crystallisation (or end of melting) to be constructed as the point where the pre-crystallisation (or post-melting) baseline meets the tangent line to the heat flux signal at its steepest point. This is the most common method of measuring onsets/endsets as it is largely independent of the operator. The repeatability of the onsets was within ± 0.1 °C.

3. MICROCALORIMETRY EXPERIMENTS

The Setaram BT 215 microcalorimeter was calibrated for temperature and enthalpy at a heating rate of 0.06 °C/min using the same standards as for the DSC. Samples of mass 500 mg were sealed into 10 ml stainless steel cells; the purge gas was dry N₂. The data was smoothed and plotted using a general graphics package and the onsets were determined manually. The repeatability of the onsets was within ± 0.1 °C.

It should be noted that the sample mass in the microcalorimeter is an order of magnitude greater than in the DSC. This factor would be important if the crystallisation process occurred by growth from a single nucleus, as for the freezing of water [4]. Then the larger volume should give less supercooling. However, in a diesel, small crystals of wax grow independently, so the volume factor is not a significant variable.

Attempts to monitor the melting of wax in the diesel using the BT 215 were unsuccessful due to a drifting baseline.

FIGURE 1. DSC curves for the crystallisation of wax from a diesel.
Cooling rates (C/min): 0.2, 0.5, 1.0, 2.0.

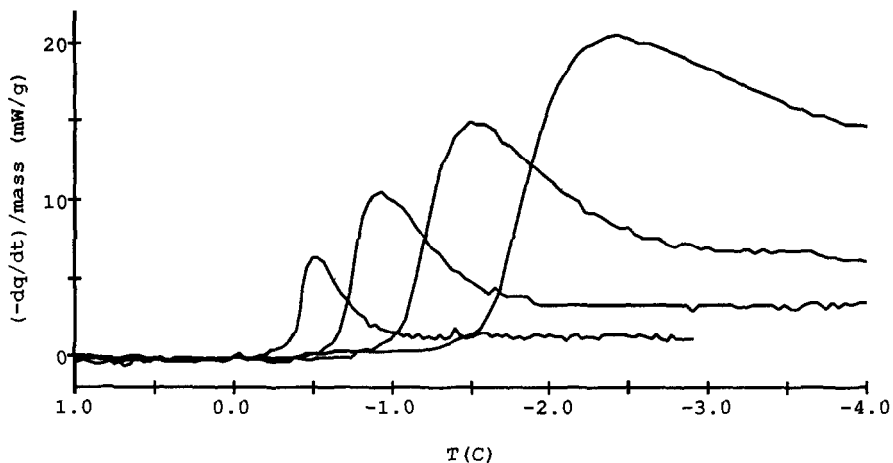


FIGURE 2. Microcalorimetry curves for the crystallisation of wax from a diesel.
Cooling rates (C/min): 0.01, 0.02, 0.03, 0.06, 0.1.

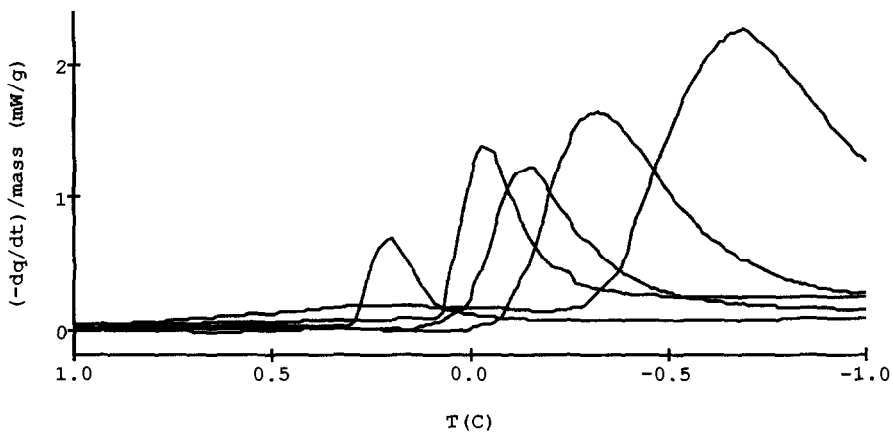


FIGURE 3. DSC curves for the melting of wax in a diesel.
Heating rates (C/min): 0.2, 0.5, 1.0.

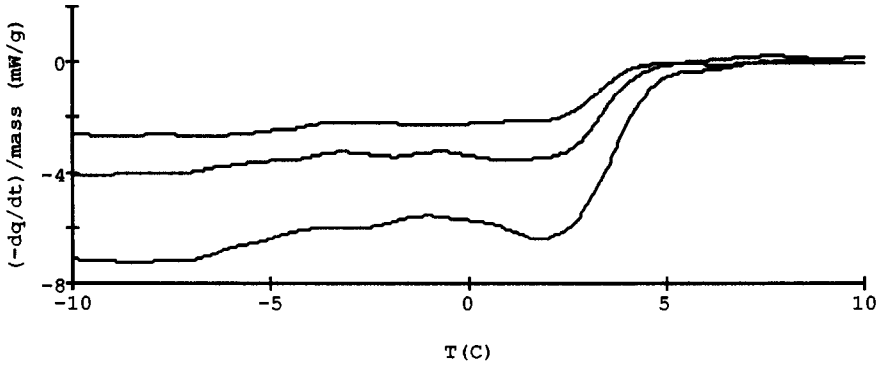
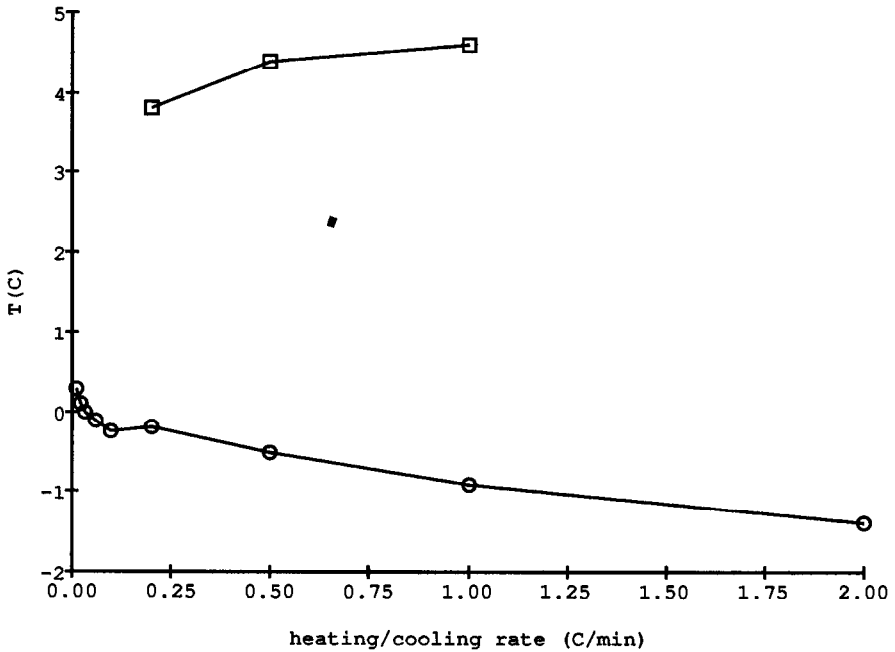


FIGURE 4. The dependence of the onset of wax crystallisation (circles) and the end of wax melting (squares) on the rate of cooling/heating.



4. RESULTS

Figures 1 and 2 show parts of the DSC and microcalorimetry curves for the crystallisation of wax from the diesel at cooling rates covering the range 0.01–2.0 °C/min. The onset temperatures are given in Table 1. Figure 3 shows parts of the DSC curves for the diesel heated from -30 °C, the relevant feature being where the endothermic signal returns to zero on the completion of melting. The end-of-melting temperatures are also listed in Table 1, and all the data there is plotted in Figure 4, except the 5 °C/min result, which is omitted to improve clarity.

TABLE 1

The effect of cooling/heating rate on the onset of wax crystallisation and end of wax melting for a diesel.

rate (°C/min)	T (°C)	Instrument
-0.01	+0.3	BT
-0.02	+0.1	BT
-0.03	+0.0	BT
-0.06	-0.1	BT
-0.10	-0.2	BT
-0.20	-0.2	DSC
-0.50	-0.5	DSC
-1.00	-0.9	DSC
-2.00	-1.4	DSC
-5.00	-2.8	DSC
+0.20	+3.8	DSC
+0.50	+4.4	DSC
+1.00	+4.6	DSC

5. DISCUSSION

From Figure 4 it is clear that the onset temperature data for wax crystallisation cannot be extrapolated linearly to give a value corresponding to a zero cooling rate; on the contrary, the curve rises steeply at the lower rates. This suggests that equilibrium conditions have not been reached, even at a cooling rate of 0.01 °C/min.

Turning to the end-of-melting data, and recognising that the amount of superheating should be small, one could extrapolate to a value of $\sim 3.5^\circ\text{C}$ at zero rate. Logically, the crystallisation temperatures should tend towards this temperature at very low rates, so the conclusion must be that the crystallisation curve will continue to rise very steeply to $\sim 3.5^\circ\text{C}$.

From a practical point of view, the crystallisation data show that, for this diesel at least, the DSC result on cooling at $1^\circ\text{C}/\text{min}$ is $< 1.5^\circ\text{C}$ lower than that from the microcalorimeter at $0.01^\circ\text{C}/\text{min}$, which is a realistic cooling rate for a vehicle. This should give confidence in the relevance of DSC results obtained at $1^\circ\text{C}/\text{min}$.

However, if the situation of interest is the transportation of crude oil in a ship, where the time scale is greater, the end-of-melting data will probably be more relevant since it is closer to equilibrium - assuming that crystallisation in a crude oil occurs as in a diesel.

6. ACKNOWLEDGEMENT

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7. REFERENCES

- 1 F.Bosselet, J.M.Letoffe and P.Claudy, *Thermochim. Acta*, 70(1983)19.
- 2 P.Claudy, J.M.Letoffe, B.Neff and B.Damin, *Fuel*,65(1986)861.
- 3 P.Claudy, J.M.Letoffe, B.Chague and J.Orrit, *Fuel*,67(1988)58.
- 4 C.Millet, Q.L.Nguyen, C.Zaffran and C.Koubanis, *Thermochim. Acta*, 67(1983)165.