APPLICATION NOTE

Differential Scanning Calorimetry

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Wax Appearance Temperature Detection by DSC

Introduction

Crude oils and natural gas fluids are composed of nearly 100% hydrocarbons. A series of naturally occurring hydrocarbons with the chemical formula C_nH_{2n+2} are known as paraffins. In most crude oils, the paraffins align as long straight chain molecules. However, they can also form branched or cyclic structures. A collection of normal paraffins, with 16 or more carbon atoms (≥C16) that form crystalline solid substances at 68 ˚F (20 ˚C), are known as wax. The amount of wax contained in a crude oil sample varies, depending on the geographic source of the crude. Whenever the temperature decreases the dispersed paraffins begin to align together. As cooling of the crude oil continues, the paraffins form a solid crystalline wax structure. The crystal growth produces high molecular weight wax, which reaches a point where it precipitates out of the crude oil. In clear crudes the wax deposition gives the oil a cloudy appearance. This temperature is called the cloud point, or wax appearance temperature (WAT).

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Since paraffins and wax occur naturally in crude oil, there is a potential for wax deposition at every step from oil production to refining. The wax deposits reduce the internal diameter of tubular transportation pipelines, restrict or block valves, and impede other production equipment. Severe wax deposition can lead to a complete stop in production; which can translate into millions of lost dollars in sales. There are many ways to remove or prevent wax deposition. For example, thermal methods include heating and insulating the pipeline or introducing hot fluids above the WAT to melt or prevent wax deposition. A wax crystal modifier can be added to the oil to prevent the wax deposition even below the WAT. However, for these two methods, their effectiveness is dependent upon the WAT.

WAT can be determined according to ASTM® D2500. In this method, the starting transparent sample oil is poured into a test jar. A thermometer is used to monitor the oil temperature. The entire jar is then put into a constant temperature bath. The cooling bath temperature is reduced by 1 ˚C step by step and the sample oil is examined visually through a microscope for crystal formation. The WAT is determined as the temperature at which the crystals first appear. This method is quite time-consuming and is not automatic – it needs the operator interaction. Another method for WAT determination is using differential scanning calorimetry (DSC). DSC measures the heat flow from or to the sample when the sample is heated or cooled. Since crystallization will give out heat, it will show up in the DSC curve as an exothermic peak during cooling. Only a small amount of sample oil is needed for DSC analysis. Since it utilizes heat to detect the onset of wax crystallization the sample doesn't need to be transparent, it can even be dark. With an autosampler, many samples can be run automatically without operator's interaction.

So DSC is an effective tool to characterize the WAT for the oil industry. It is also useful to optimize chemical treatment parameters for cost-effective wax control, including selecting optimal wax crystal modifier and treatment formulation. In this paper, the Diamond DSC from PerkinElmer is used to determine the WAT of an oil sample.

Experiment

Once a sample of crude oil or a wax deposit is received from the well site, it is prepared for analysis. Figure 1 shows the crude oil sample above WAT on the left and crude oil sample below WAT on the right. After transferring the sample into a thermally safe container, the crude oil is heated in an oven at 80 ˚C for 2 hours. This will ensure that the suspended waxes will be melted. Once the crude oil is thoroughly heated, a 30 micro-liter sample is injected into the DSC stainless steel hermetic pan (Figure 2). The o-ring and lid are inserted on top of the pan and compressed to form a seal. The hermetically-sealed pan will prevent any evaporation of oil at high temperature. The temperature parameters are set for a typical maximum temperature of 120 ˚C to a minimum of -20 ˚C at a rate of 10 ˚C/minute in the DSC method.

The instrument used here is a double furnace DSC from PerkinElmer with an autosampler (Figure 3). This features the proprietary double furnace power com-pensation design. It offers highly sensitive and accurate temperature and heat flow measurement.

Figure 1. Crude oil sample above WAT (left) and crude oil sample below WAT (right).

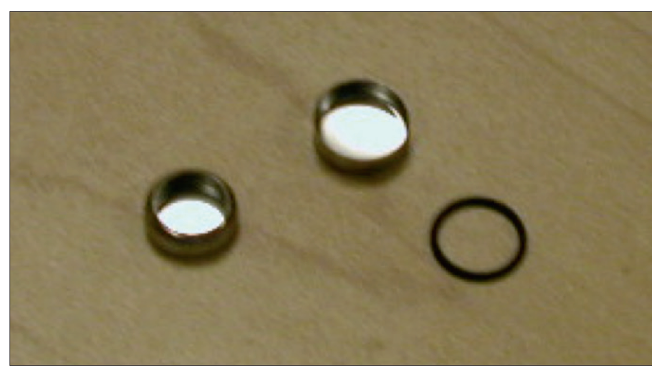

Figure 2. Stainless steal pan (Part Number 03190218) used for this experiment.

Figure 3. DSC 8000 with autosampler.

Results

Once the DSC has completed the test, a graph will be produced for each analysis performed. It will require the operator to take a more in depth look in order to find the desired information. As the oil sample is cooled from the maximum temperature, the heat trace measures the energy at each temperature. Once the paraffins align themselves and begin to form crystals, energy in the form of heat is given off. The exothermic reaction of crystallization is recorded. This temperature is determined to be the wax appearance temperature (WAT).

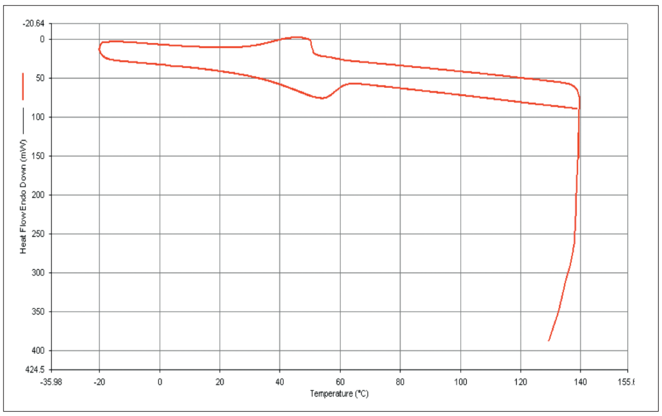

Figure 4. DSC Heat Flow curve.

In order to locate the wax appearance temperature, only the cool down portion of the Heat Flow curve is selected. It will allow for magnified viewing of the curve, as well as additional analysis.

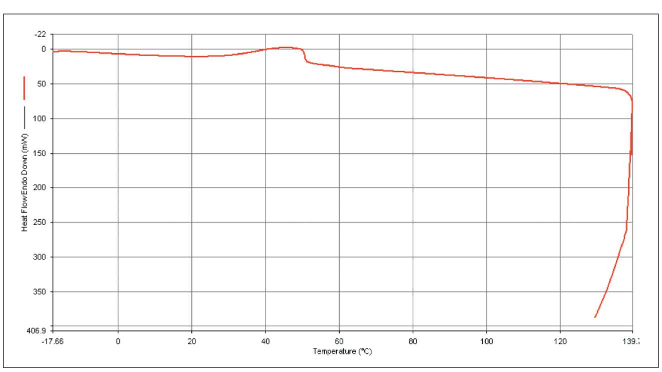

Figure 5. Heat Flow Cool Down curve selected view.

In cases where the start of crystallization is not obvious on the Heat Flow Cool Down curve, the first derivative can be very helpful. By looking at the derivative plot of the curve, we are able to zoom in on the defined exothermic peak of the curve.

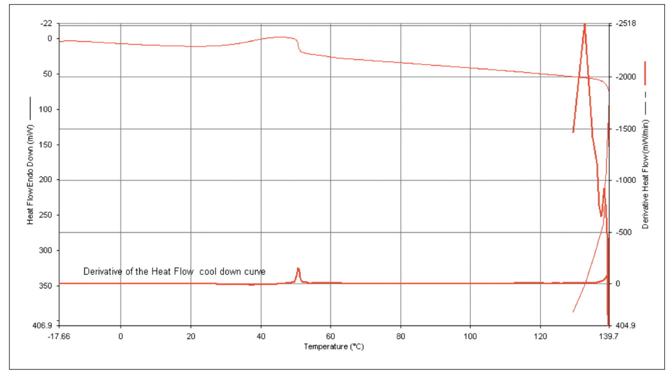

Figure 6. Derivative curve of the Heat Flow Cool Down curve.

The derivative process produces a series of peaks and troughs in this region, and the onset of this area of instability denotes the beginning of crystallization. After magnifying the curve, the Onset temperature is ready to be calculated. The Onset temperature is denoted by the section of the curve where the heat flow begins to decrease as the oil sample gives off heat energy.

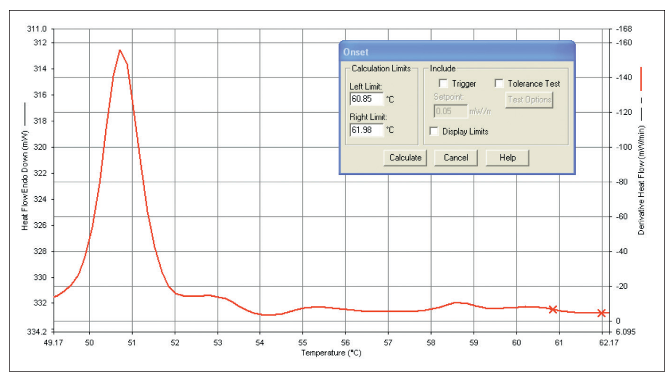

Figure 7. Onset calculation using the derivative curve.

The Onset temperature is calculated by adjusting the lines to find the tangent point where the slope changes. The calculated temperature will be noted as the Wax Appearance Temperature.

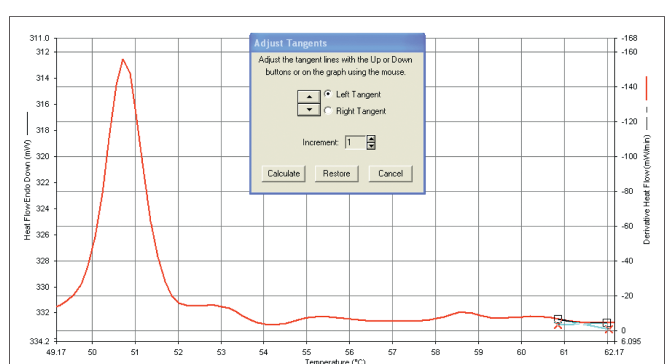

Figure 8. Adjustment of tangent arms in order to calculate the onset.

The recorded temperature of the Onset temperature will be denoted on the Heat Flow curve.

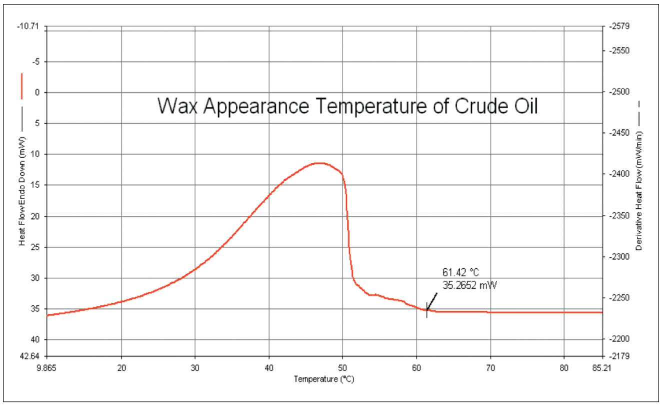

Figure 9. Notation of wax appearance temperature on Heat Flow Cool Down curve.

Conclusion

The DSC is a very important tool for the oil field industry. Its capabilities allow for the measurement of the Wax Appearance Temperature, which is used to predict and prevent the occurrence of wax deposition. The DSC's ease of use, multi-sample capability, and powerful analysis software make it an ideal measurement tool.

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