AN697

ENERGY AND ENVIRONMENT
GAS HYDRATES & FLOW ASSURANCE

Effects of pressure on the Wax Appearance Temperature (WAT) of crude oils

INTRODUCTION

In the petroleum industry, waxes crystallization resulting from the precipitation of paraffins contained in oils, can occur in reservoirs, pipelines and process equipment. Many major issues can be related to these deposits, including a modification of the flow characteristics, a reduced production or even a blocked line in the worst cases. To evaluate the possible wax precipitation of a given fluid, the wax appearance temperature has to be determined. It is defined as the temperature at which a crude oil first precipitates. Most of the studies about WAT are carried out under atmospheric pressure. However, WAT determination under experimental conditions close to real operating ones (particularly under pressure) is a key point to predict the crude oils behavior.

EXPERIMENT

The high-pressure microcalorimetry analyses were carried out with the MICROCALVET, using two 330 µL Hastelloy C276 cells (sample and reference) designed to undergo pressures up to 400 bar. Two different crude oils, A and C, have been studied. They were preheated at 80°C for 1 hour to make sure waxes were solubilized. After cooling, about 100 mg of each sample were transfered to the MICROCALVET and analyzed using the following profile:

Figure 1 – Example of wax deposits in a pipe

- heating from 30°C to 80°C and isotherm of 180 minutes at this temperature,
- cooling at 1°C/min until reaching a temperature of -10°C and isotherm of 15 minutes at this temperature,
- heating at 1°C/min from -10°C to room temperature. A quantity of undecane was placed in the reference cell to keep the calorimeter balanced. Two gases were used for pressurization: methane (99,995%) and nitrogen (99,996%). To determine the samples WAT, the onset temperature of the first peak has been considered. It is defined as the intersection between the baseline and the tangent at the first peak inflection point (figure 2).

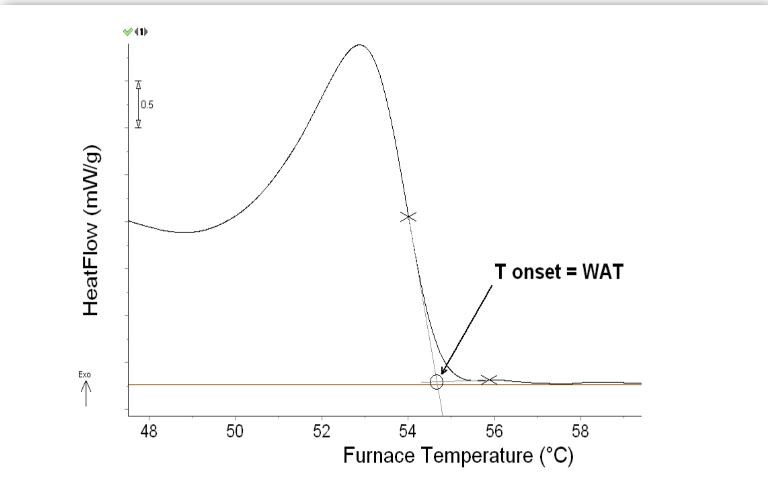

Figure 2 –WAT determination

	A	C
Paraffins content (wt %)	5,4	3,1
Linear parrafins above C34 (wt % of n-paraffins)	16	15

Table 1 – Samples content

RESULTS AND CONCLUSION

Before pressurization, the experiments were run at amospheric conditions (1,01 bar). Two exothermic events were recorded for each sample during the cooling phase corresponding to two different paraffinic fractions that precipitate (high molar masses first then lower). The WAT, related to the first peak, was found at 44.6°C for the sample A and 44.2°C for the sample C.
The pressurization of the two oils in presence of a rising pressure of nitrogen increased the WATs (see figure 3). On the contrary, with methane, crystallization temperatures were reduced for both samples (figure 4) leading to the conclusion that methane, unlike nitrogen, plays a role in improving the solubilization of waxes. This tendency to see the WAT reduced under methane pressure was even more significant with the sample C. It can be explained by the fact that it contains a lower paraffin content and above all less linear paraffins above C34 than the sample A (table 1).

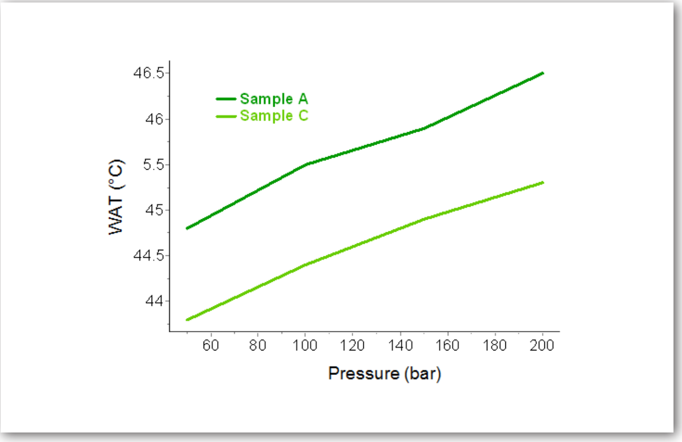

Figure 3 – WAT vs nitrogen pressure for both samples

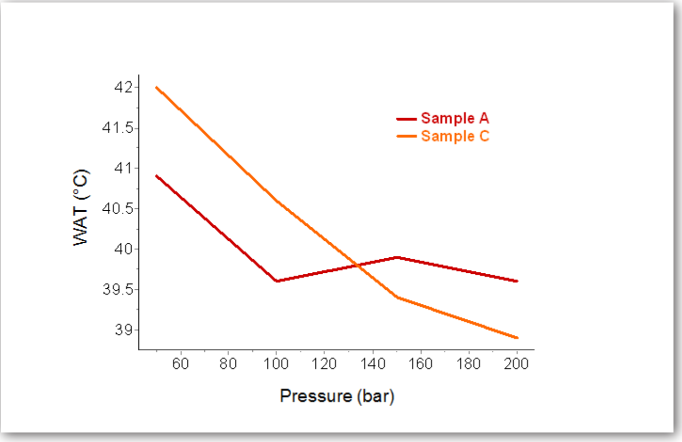

Figure 4 – WAT vs methane pressure for both samples

A further data exploitation is possible with Calisto data treatment software to determine the percentage of converted waxes versus temperature (if the heats of crystallization of the "pure" waxes are known).

Reference: ASTM E1641-13 Standard test method for decomposition kinetics by thermogravimetry using the Ozawa/Flynn/Wallmethod.

INSTRUMENT

MICROCALVET

-45°C to 120°C

HIGHEST HEAT MEASUREMENT ACCURACY
3D sensor based on thermocouples with Joule effect calibration.

MODIFIABLE TEMPERATURE CONDITIONS
for increased flexibility and replication of real life conditions.

CONVENIENT INTERCHANGEABLE CRUCIBLES AND CELLS
to perform even the most demanding experiments using one instrument :

- high pressure (1000bar) and high vacuum
- pressure measurement and control
- mixing experiment

EXTERNAL COUPLING CAPABILITY
designed to increase your research options including manometry, BET instrumentation, gas analyzers, humidity controllers and gas panels