

THE LIMITATIONS OF THE CLOUD POINT MEASUREMENT TECHNIQUES AND THE INFLUENCE OF THE OIL COMPOSITION ON ITS DETECTION

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ABSTRACT

Cloud points are in the petroleum industry one of the main guides to evaluate the wax precipitation potential of a fluid. The planning of the exploration of a reservoir or the design of its pipelines are based on the measured cloud points for the reservoir oil. It is known that each measuring technique will provide a different cloud point temperature, yet although some of these techniques seem to be more accurate than others no definite conclusion has been established on how cloud points should be measured.

On this work several cloud point measurement techniques are discussed and compared. It will be shown that some of these techniques such as viscosity, filter plugging and DSC can only be used under very favourable circumstances but it will be argued that since every technique requires some finite, often large, amount of solid to detect the presence of a new phase, the cloud point, defined as the temperature for which the first solid appears in the oil, is not accessible experimentally and, unless a very detailed compositional analysis is available, it is also impossible to predict it accurately with a thermodynamic model. The effect of the paraffin distribution in the oils on the cloud point detection will be discussed and it will be shown how the compositional information can be used to assess the uncertainty of the measured cloud points.

INTRODUCTION

Wax formation in crudes and its deposition on reservoirs and pipelines constitutes a major problem in the extraction and transportation of petroleum in offshore. The paraffins precipitate from the liquid matrix mainly due to the cooling of the fluid as it is extracted from the reservoir but changes in composition due to losses in light compounds to the gas phase caused by pressure depletion also contribute to the wax formation. The potential of a fluid to wax precipitation is measured by the cloud point of the fluid. The cloud point, a.k.a. wax appearance temperature, is defined as the temperature at which the first solid particles appear in a fluid. Several methods to measure the cloud point have been proposed and a number of them became ASTM

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standards (e.g. ASTM 2500-98a (1998); ASTM 3117-96 (1998)). The methods differ in the cooling program used but their main distinction is the method of detection of the first crystals. In a review of the methods used for cloud point determination it will be shown how these methods are dependent of the quantity of solid required to produce a detectable signal and how this can affect the cloud point estimation by as much as 20 K. The influence of the oil composition on the cloud point measurements will be examined. It will be discussed the possibility of a model to predict the cloud point from compositional information alone showing how the cloud point estimates are very much dependent on the composition of the very heavy paraffins that can hardly be measured and are seldom available. It will be concluded that the true cloud point, i.e. the temperature at which the very first crystal of paraffin is formed in a fluid, is probably not accessible experimentally and, alone, is not a good indication of the hazardous potential of crude oils.

HOW WAX FORMS IN PETROLEUM FLUIDS

If the cloud point is defined as the temperature for which the very first crystal of paraffin appears in the fluid then this temperature will depend on the total wax content, the paraffin distribution and the heaviest paraffin present on the oil. It may be somewhat surprising and counterintuitive but the oil nature that could be described by a PNA or a SARA analysis does not influence significantly the cloud point as discussed by Coutinho and Daridon (2001). The presence of asphaltenes has not been proved to have any influence on the cloud point besides becoming crystallisation nuclei (Garcia and Carbognani, 2001). Using a model shown to be successful in describing wax formation and cloud points of crudes and distillate fractions (Pauly et al., 2000 and 2001; Coutinho and Daridon, 2001; Mirante and Coutinho, 2001; Coutinho et al., 2002), five hydrocarbon mixtures that emulate real crudes in what concerns the main characteristics enounced above (wax content, paraffin distribution and heaviest paraffin present) are simulated. Compositional information for these mixtures is presented in Table 1. Paraffin distribution and heaviest paraffin present were chosen to be closely related to real oils (Monger McClure et al., 1999). Simulated results for the wax fraction formed are presented in Fig.1. It is clear that the heaviest paraffin present in the oil has a dramatic effect on the cloud point and the heavier this is the more difficult will be to detect the true cloud point that often will appear at the top of a very long and thin tail.

CLOUD POINT MEASUREMENT TECHNIQUES

Numerous experimental techniques have been proposed, patented and adopted as standards. In face at the huge number of techniques available it would be tempting to suppose that cloud points are easily measurable and that adequate methods for their determination are available. The problem with cloud point measurement techniques is that no technique available seems to be able to detect the very first crystal to appear in a representative fluid sample in thermal equilibrium. All techniques will require some amount of solid to be present to produce a detectable signal. Several techniques use

temperature-scanning rates that prevent the sample from being in thermal equilibrium thus adding a further error to the measurement. Finally some techniques produce signals which interpretation is not straightforward.

ASTM Standard Methods

The ASTM methods for determination of the onset temperature of wax crystallisation (D2500 and D3117) rely upon the visual inspection of a 30 mm thick sample to detect crystal formation. This method presents multiple weaknesses in what concerns the cooling rates, temperature measurements and the subjective judgement of the operator on the cloud point. Even when an automatic optical device replaces the operator, increasing the reproducibility of the measurements, the amount of solids required for a change in appearance of the oil to take place or for a detectable signal to be produced may still be quite important. Besides these methods can only be used for refined products or clear oils such as gas condensates and not to black oils. The use of optical devices with other than visible light is discussed below.

DSC

Thermal methods are quite popular to determine the cloud point of petroleum fluids due to the high enthalpies of crystallization of the paraffins. Among these DSC is the mostly used. Based on the precipitation curves presented in Fig. 1 simulated DSC curves were calculated and the cloud points assessed as the crossing point between the tangents to the peak and the baseline (ASTM D4419-90, 1998; Kok et al., 1996). Results are presented in Figs. 2a-d. It shows how the quality of DSC cloud points is dependent on the paraffin distribution. Comparison between oils A,B and C, D shows that the heavier is the higher paraffin present the longer are the tails and then the farther from the true cloud point will the measurement be. For oils with very heavy n-alkanes such as oils A, C will be more difficult to detect the true cloud point but the cloud point, although with a larger error, is determined for a much lower quantity of solid precipitated than for oils B, D. This result is in agreement with the conclusions of Kok et al. (1996). In all studied cases using DSC both the errors in the cloud point temperature and the amount of solid required for a change in signal to be detected are important. Simulated DSC's suggests that instead of tangent interception the deviation from the baseline would be a more precise method to detect solid formation, however in real DSC measurements a good base line may be difficult to obtain and the deviation from the baseline difficult to assess. Moreover, due to its dynamic character, it is not only the crystallisation of wax that is responsible for the signal but also the rate of crystallisation. Very low rates of crystallisation will be offset by the baseline drifting and noise, or simply will be difficult to identify, such as in oils A and C, thus the quality of the measured cloud points will be very much fluid dependent.

DSC has still the problem of being a dynamic method requiring a temperature-scanning rate to be used that often is far too large for a thermodynamic equilibrium to be

achieved and thus important supercooling of the sample occurs. Superheating, as discussed below, is less prone to occur and important differences between wax appearance temperatures (WAT) and wax disappearance temperatures (WDT) are reported (Rønningsen et al., 1991; Monger McClure et al., 1999). The differences between WAT and WDT may be due not only to the supercooling effect but also to poor DSC calibration. As shown by Martins and Cruz-Pinto (1999) the failure to calibrate the DSC on cooling and the use of calibrations on heating for measurements on cooling is responsible for many errors on the temperature measurements using a DSC. The low cooling rates required for thermodynamic equilibrium to be achieved cannot be used in DSC as the signal becomes too weak and the noise of the measurement overshadows the thermal effects (Jiang et al., 2001). The cloud point comparison using different techniques presented in Table 2 gives a good indication of the limitation of this technique although it is interesting to remark that an experienced user of DSC can obtain cloud points by DSC higher than by CPM as reported by Kok et al. (1996).

The application of the Temperature Modulated Differential Scanning Calorimetry (TMDSC) to the measurement of wax appearance temperatures has been done by Jiang et al. (2001) but the results reported do not seem to improve over the conventional DSC.

Viscosity

Determination of Cloud Points through viscosity changes is a technique used by several authors (Rønningsen et al., 1991; Erickson et al., 1993). Due to the formation of wax crystals in suspension the fluid develops a non-newtonian behaviour with temperature. Newtonian fluids follow an exponential temperature dependence of the Arrhenius type known as the Andrade equation

$$\mathbf{h} = \mathbf{h}_o \exp\left(\frac{E_a}{RT}\right) \quad (1)$$

the cloud point could thus be detected by a deviation of the experimental data from linearity in a $\ln \eta$ vs. $1/T$ plot.

The dependence of viscosity on the amount of solids in dilute suspensions is given by the Einstein equation:

$$\mathbf{h} = \mathbf{h}_f (1 + 2.5\Phi) \quad (2)$$

In the following analysis the crystals are assumed to be spherical and, since the density of the solid wax is not much different from the fluid, the volume fraction is taken to be similar to the mass fraction. If a deviation of 2.5% from the newtonian fluid viscosity is required to detect a non-newtonian behaviour, and this is a conservative estimate given the exponential dependence of the viscosity on the temperature, this corresponds to a mass fraction of crystals of 1%! This value of solids is often enough to produce a pour

point and not the cloud point (Claudy et al., 1993; Coutinho et al., 2002; Coutinho et al., 2003; Lopes da Silva and Coutinho, 2004).

The viscosity cloud point cannot thus be detected within the dilute region. Only when the volume fraction of crystals is large enough for the viscosity to increase no longer linearly but exponentially will a change in signal be large enough to be detected. The critical volume fraction that separates the dilute and semi-dilute regions is (Cazaux et al., 1998)

$$\Phi = \left(R/L\right)^2 \quad (3)$$

Although no exhaustive study has ever been present in the literature the evidence available from microphotographs indicate that the paraffin crystals have axis ratios of about 15-20. This would mean critical volume fractions of 0.3-0.5%. This value is in close agreement with the values proposed by Rønningsen for the mass fraction of paraffins at the viscosity cloud point (Rønningsen et al., 1991). This amount of solids may seem small but even very small amounts of solids can represent serious production problems. With only 0.5 wt% solids detected in the laboratory more than 600 Kg of solid phase will be formed in the field for every 1000 bbl produced (Thomas and Bennion, 1999) Unlike DSC this technique seems to detect cloud points using a coherent solid volume fraction. Although the measured cloud point would be quite far from the true cloud point it would present a lower error for oils with paraffin distributions similar to oils B, D than to oils A, C.

Filter Plugging

This technique is based on the continuous monitoring of the pressure drop across a filter while the oil flows through a temperature controlled flow-loop. It has quite a number of interesting features since it is applicable to both live and dead oils at low or high pressures unlike most of other techniques that are restricted to dead oils at low pressures. Filters with a 0.5 μm are commonly used along with very low flow rates (inferior to 0.5 cm^3/min) to minimize the shear stress at the filter promoting the deposition and the pressure build-up.

Using the Carman-Kozeny equation to describe the flow in porous media (Foust et al., 1980) it is possible to show that the pressure drop across a filter is proportional to the cube of the inverse of the porosity, ϵ^{-3} , and thus to the cube of the solids concentration, w_s^3 :

$$\Delta P \propto \epsilon^{-3} \propto w_s^3 \quad (4)$$

Figure 3 shows the pressure drop with the temperature for oils A-D. The exact cloud point temperature would be dependent on the accuracy of the pressure measurements but it is clear that the temperature identified would be not far from 320 K for oil A or even lower, this is to say an amount of solid of 1%, probably closer to the pour point than the cloud point as mentioned before.

A significant quantity of crystals with size larger than 0.5 μm must develop before the filter plugs. Filter plugging cloud points must thus be dependent on the flow rate used. The higher the flow rate the more difficult will be for large particles to form and to deposit in the filter since the shear stress produced by the flow will contribute to reduce the size of the particles increasing the quantity of solid required to plug the filter and thus reducing the measured cloud point.

Light Transmission Measurements

Multiple light transmission techniques have been proposed to detect the Cloud Point. It minimizes the uncertainty associated with the visual inspection techniques and depending on the light source used can be applied, unlike ASTM standards, to black oils. It measures the variation on light transmission due to the appearance of crystals as the sample is cooled. It seems to improve the results over the visual inspection technique (Kruka et al., 1995) but an important quantity of crystals must be required to produce a detectable reduction on the light transmitted since Hammami and Raines (1997) reported that differences on the order of 10 K between light transmission and CPM are found. McMullin et al. (1999) remark that 'the drop in transmission of laser light through a sample does not actually measure the wax appearance temperature but rather the initiation of the growth stage'.

The simulation of a light transmission curve as was done to DSC and filter plugging is too complex to be attempted. At the beginning of the precipitation crystals can be assumed independent and small enough for the Beer's law to be used in the description of the attenuation of light due to scattering. However as temperature drops there is an increase of not only the crystal number but also of the crystal size and shape and aggregation of crystals into a 3D network. The extinction coefficient must then also change due to these factors and quickly the crystals become too large compared too the wave length so that Beer's law is no longer valid. The shape of the curves presented by Hammami and Raines (1997) do not show the exponential decay of Beer's law but a sudden drop on the light transmitted and the photomicrographs presented by Hammami indicate that the size of particles is more than 20 times the wavelength of the radiation used. The drop in signal will thus be produced by large crystal aggregates and not the small crystal particles leading to important cloud point detection errors.

Since the light transmittance can be measured across a high-pressure cell this method has been used to measure high-pressure cloud points.

Acoustic Resonance Techniques

Acoustic resonance techniques for the determination of the appearance of a solid phase in oils have been proposed (Ruffier-Meray et al., 1993; Colgate and Sivaraman, 1996; Sivaraman et al., 1999 Carrier et al, 2000). These techniques have not yet been extensively compared against other conventional techniques and the response to the

presence of a new solid phase appears to be of some complexity requiring some experience to be able to distinguish between the different signals (Sivarman et al., 1999). Like the precedent this method has been extended to high pressures and to the analysis of live oils. The results available indicating that it may be more sensitive than IR techniques (Sivarman et al., 1999) are too scarce. Our personal experience with this technique for wax appearance temperatures is not very favourable. The interpretation of the signal output is not straightforward and the measurements do not seem to be reproducible and large fractions of solid are required for a detectable change in the signal to occur due to the very small size of the crystals comparing to the wavelengths used.

IR techniques

The Cloud Points are measured by detection of the increase in energy scattering due to the wax solidification. The wavelengths used may vary with the approach and live oils at high pressure can be studied with this technique. Although in a comparison of cloud point measurement techniques FTIR consistently produced the most conservative values (Monger-McClure et al., 1999) even in comparison to CPM it would be to go too far to say that this is the most sensitive technique for cloud point detection. Indeed their microscopy values seem to be underestimated when compared to the calorimetric values. The most extensive application of FTIR to measurement of wax formation in oils was developed by Roehner and Hanson (2001). The determination of the cloud point is obtained by identification of a break on the absorbance of the $735\text{--}715\text{ cm}^{-1}$ peak area with temperature. The problem, akin to what happens with the DSC, it is the identification of the linear regions to obtain the cloud point by intersection of the two lines. For model systems when a large amount of solid forms in a narrow temperature range below the cloud point it is easy to identify the cloud point and the limits of the linear region. This may be far more complex for fluids with long n-alkane distributions and with low total n-alkane content where the precipitation of the solid is very gradual and the departure from the linear base line is subtle and difficult to detect. In particular for the TAPS Mix reported by Roehner and Hanson (2001) it is clear that the liquid base line is very dependent on the number of points used to define it. The choice of the absorbance points and the regression used influences significantly the cloud point measured. As discussed above for other techniques, for oils with very small amounts of solid forming just below the cloud point, the effect of the solid formation on the FTIR spectra it is within the sensitivity of the experimental method.

Cross Polarization Microscopy (CPM)

CPM is one of the most widely used Cloud Point techniques and one that seems often to give the most conservative results for Cloud Point measurements when carefully applied. It is based on capacity that wax crystals, unlike liquid hydrocarbons have, to rotate the plane of polarization of transmitted polarized light. The limit of detection is a crystal with a size between 0.5 and $1\text{ }\mu\text{m}$ depending on the magnification used. It should

be more accurate than the filter plugging technique since it can detect particles with a similar size but in much less quantity since a single crystal is enough to be detected. CPM seems to be sensitive to the thickness of the film used (Rønningsen et al., 1991) and different authors have been using different approaches from no spacer as in Monger-McClure et al. (1999) to 50 μm of Rønningsen et al. (1991) and the 150 μm of Cazaux et al., (1998) what may contribute to uncertainties on the evaluation of the technique. Moreover given the very small sample volume used the sample may not be representative and the restricted field view may also difficult the detection of the first crystals. Although typically used for low pressures, this technique has been extended to high pressures using a high-pressure microscope stage, (Brown et al., 1994; Daridon et al., 2002).

Recent results on the morphology of paraffin crystals in crude oils using transmission electron microscopy (Kan   et al., 2003) indicates that the first crystals forming under quiescent conditions have sizes of just 50 nm in length and a thickness of about 2-3 nm with aggregates forming with a size of 150 nm. Under shear the size of individual crystals is about 20-30 nm and aggregates have no more than 100 nm. These are well below the detection limit of the CPM technique. The size of crystals forming on oils is much smaller than in synthetic mixtures or refined products such as diesels. Although some of this can be attributed to the complexity of the mixture crystallizing as discussed by Anderson et al. (2001) alone this effect cannot explain the extremely small size of the crystals. This must be due to the presence of natural crystal growth inhibitors present on the oil that prevent the growth of the crystals. This may also explain the poor behavior of CPM for some oils although in general it seems to be one of the most conservative techniques for measuring cloud points.

A number of other methods based on densitometry (Kruka et al., 1995), X-ray (Karacan et al., 2000) and other techniques have been reported or patented. In general all the cloud point methods suffer from limitations akin to those discussed above such (Kruka et al., 1995), either the crystals must be large or a large quantity of crystals is required.

TESTING MEASUREMENT TECHNIQUES USING N-ALKANE SOLUTIONS

Often, techniques proposed for cloud point detection, are tested using solutions of one or a few n-alkanes to emulate the wax formation in real fluids (Majeed et al., 1990; Ruffier-Meray et al., 1993; Monger-McClure et al., 1999). This approach is not acceptable since cloud point detection techniques often rely on the rate of appearance of crystals or on the quantity of solid to detect a new phase. Most techniques perform very well for high rates of precipitation and when important quantities of solid form just below the cloud point. These conditions are easily met by simple synthetic solutions of n-alkanes but, as shown in Figure 1, although waxes are constituted by n-alkanes due to the long paraffin distribution they do not behave on this way and thus the ability of a technique to detect n-alkane crystallisation on a synthetic mixture is by no means guarantee of success in the detection of cloud points of real oils. Moreover the paraffin crystal size distribution is strongly influenced by the complexity of the alkane mixture as shown by Anderson et al. (2001). Methods that rely on the size of the wax crystals to

detect the cloud point will report good results for simple mixtures for which large crystals may grow but not necessarily for complex mixtures for which the crystals will have much smaller dimensions.

EFFECT OF THERMAL HISTORY AND SCANNING RATES

The simulated curves used in the previous analysis are the curves for equilibrium conditions and was shown that, even under equilibrium, measured cloud point temperatures may be far from the true cloud point. The generality of the essays are however done not under static conditions, but under dynamic conditions. In some cases the temperature scanning rates (0.1-0.5 K/min (Hammami and Raines, 1997; Sivaraman et al., 1999; Monger-McClure et al., 1999)) are low enough to consider that deviations to equilibrium are negligible if the sample cell is small enough but often very large scanning rates (5-10 K/min (Rønningsen et al., 1991; Erickson et al., 1993; McMullin et al., 1999)) are used leading to considerable superheating/cooling effects. An empirical correction in cloud point temperatures equal to the cooling rate in K/min has been used (Monger McClure et al., 1999) but the results reported by Rønningsen et al. (1991) indicate that this effect may be much more important. Moreover most of these techniques use cooling cycles rather than heating cycles in the determination of the cloud point and sometimes the cooling rate is not constant such as in ASTM D2500. Due to difficulties associated with crystal growth, detection of crystal formation in cooling cycles is far less rigorous than under a heating cycle. Determination of the melting of the last crystal is easier and more reproducible than the formation of the first crystal. Evidence for the differences between wax appearance temperatures (WAT) and wax disappearance temperatures (WDT) using DSC (circa 15 K) and microscopy (circa 10K) clearly express this problem often associated to important supercooling effects due to the large cooling rates used. Interestingly data by Rønningsen et al. (1991) on WAT and WDT differences support the analysis of the cloud points' dependence with the paraffin distribution done on this work. It would be reasonable to expect that faster paraffin decays, with the long precipitation tails, would have more difficulties in crystallise and thus produce larger WAT-WDT differences. This is what the data by Rønningsen presented on Figure 4 reveals. Recently Bhat and Mehrotra (2004) established the WDT as the thermodynamically variable showing this to be the appropriate measure for the liquidus temperature of wax-solvent mixtures or crudes.

EFFECT OF CRUDE OIL SAMPLING, SAMPLE HANDLING AND TREATMENT

The analysis of the cloud point measurement techniques reveals the importance of the paraffin distribution, and the limits of this distribution on the wax formation. Noticing that most of measured cloud point of waxy crudes (Rønningsen et al., 1991; Monger-McClure et al., 1999) are around 315 K, and that, as this study has shown, true cloud points are probably even larger, it is easy to realize how oil sampling, sample handling and sample pre-treatment may have a huge influence on the measured data. Most of the published data are measured properties of crude oils collected at the separator. These

types of fluids may not be representative of down hole fluids if the true cloud point temperatures are above those maintained at the separators (i.e., heaviest paraffin molecules would likely drop out or stick to the production tubing and not reach the separator as the temperature cools down from the well bore to the well head and eventually the separator). Oil A will be taken as example. If during sampling this oil was cooled to a temperature of 320 K it would have lost all the paraffins above C50 turning into oil E. The resulting oil would have a completely different cloud point and precipitation curve as shown in Figure 1. Lost of this material would hardly be detected. The reduction in total wax content of about 1% is within the accuracy of experimental techniques. Results obtained from this sample would be completely meaningless in what concerns identification of depth of deposition on the field or amount of precipitated wax. Such a loss of heavy material can easily occur at any step given the cloud point temperatures of crudes being well above room temperature. For obtaining a representative sample and meaningful measurements utmost care must be taken during sampling, sample handling and measurements not to loose any heavy material. This analysis is in accordance with the recommendations of Monger-McClure et al. (1999).

MODELING OF CLOUD POINTS

A number of models have been reported on the literature to describe the cloud point of oils (Coutinho et al., 2004). They are usually based on the thermodynamic description of the solid liquid equilibrium of heavy paraffins and although some claim being predictive generally these models are fitted to experimental data, typically to cloud points that are the most commonly available data for the low temperature behavior of oils. Given the uncertainties associated with the cloud point measurements discussed above it is not surprising that models fitted to experimental cloud points cannot produce an adequate description of the wax precipitation in the oil. As discussed above an adequate description of the wax formation of an oil by a thermodynamic model requires a detailed description of the oil composition in what concerns the paraffins present: 1-total amount of paraffins, 2-paraffin distribution and 3-largest paraffin present in the oil on a concentration above its solubility threshold. Figure 1 clearly shows the effect of these three quantities on the wax precipitation curves. If for large paraffin decays (C_{n+1}/C_n below 0.9) the heaviest paraffin influences only the cloud point but not significantly the wax precipitation curve for small paraffin decays (C_{n+1}/C_n above 0.9) the knowledge of the large paraffin changes not only the cloud point but also the precipitation curve itself. A detailed composition analysis is thus not only a tool for the analysis of the cloud point reliability along the lines discussed above but also a must for an adequate modeling of wax formation and thus of wax deposition from live or dead oils.

That paraffin distributions have such a dramatic effect on cloud point measurements and modeling is well illustrated by a counter-example. Although cloud points for crudes are quite difficult to measure or predict, cloud points for refined products such as jet fuels or diesels have their cloud points easily detected and their modeling is easy and quite reliable (Coutinho, 2000; Mirante and Coutinho, 2001). Due to the narrow paraffin distributions on these fluids, and very large paraffin decays (typically of about 0.5) the

solubility threshold of heavy paraffins is quickly attained leading to a fairly well defined and well behaved system.

CONCLUSIONS

The paraffin distribution on crude oils and its breadth has a dramatic effect on the wax formation and in particular on the detection of cloud points. Oils with paraffin distributions leading to the precipitation of large quantities of solids just below the cloud point can have their cloud points easily identified and most techniques are adequate to their measurement. Unfortunately most oils have very low precipitation rates close to the cloud point making difficult a reliable measurement of the cloud point. It has been here shown that all the currently available techniques present shortcomings that prevent the detection of the true cloud point and that the incertitude of the measurements is as much oil as technique dependent since the error is not only associated to the technique but also to the oil composition. Due to the poor reliability of the cloud point measurements they shouldn't be consider alone as a good indicator of the hazardous potential of a crude oil. Nevertheless a detailed compositional analysis, when available, can provide an insight on the accuracy and reliability of the cloud points measured using different techniques and other information can complement or replace cloud points in the evaluation of the wax formation potential of an oil with advantage as discussed elsewhere (Hammami et al., 2003).

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Table 1 Oil compositions

Fluid	Total wax content/%	Mw	Solvent	Paraffin decay (C_{n+1}/C_n)	Heaviest n- alkane
Oil A	15.0	230	C15	0.92	90
Oil B	15.0	230	C15	0.92	50
Oil C	15.0	230	C15	0.88	90
Oil D	15.0	230	C15	0.88	50
Oil E	13.77	230	C15	0.92	50

Table 2 Comparison of cloud point detection techniques. Average temperature differences and standard deviations (*in italic*) reported between the technique on the line and the technique on the column.

	Viscosity	DSC	Light transmittance	Filter plugging	ASTM 2500	Acoustic	FTIR
CPM	6.0 (4.7) ^a , 13.2 (8.4) ^c , 5.4 (6.9) ⁱ , 0.7 (3.9) ^l	9.0 (6.9) ^a , 14.6 (9.7) ^c , 1.3 (3.1) ^e , 6.0 (7.8) ⁱ , -1.2 (5.2) ^l	10.4 (0.6) ^b	6.1 (4.7) ^d , 0.1 (3.1) ^e			-1.8 (3.6) ^e
viscosity		3.0 (5.6) ^a , 1.0 (3.6) ^c , 0.7 (0.9) ⁱ , 2.9 (4.0) ^h , -1.9 (7.2) ^l			-4.4 (-) ^f		
DSC				-1.2 (2.5) ^e	-5.6 (-) ^f , -5 (8.9) ^j , -3.8 ^k		-3.1 (2.9) ^e
Light transmittance					2.8 (-) ^f		
Filter plugging							-1.6 (3.4) ^e
ASTM 2500							
Acoustic							2.2 (0.6) ^g
FTIR							

^aRønningsen et al. (1991); ^bHammami and Raines, (1997); ^cErickson et al., (1993) ^dRønningsen et al. (1997); ^eMonger-McClure et al., (1999); ^fKruka et al., (1995); ^gSivarman et al. (1998); ^hElsharkawy et al., (2000); ⁱCazaux et al., (1998); ^jNoel (1972); ^kClaudy et al. (1986); ^lKok et al. (1996)

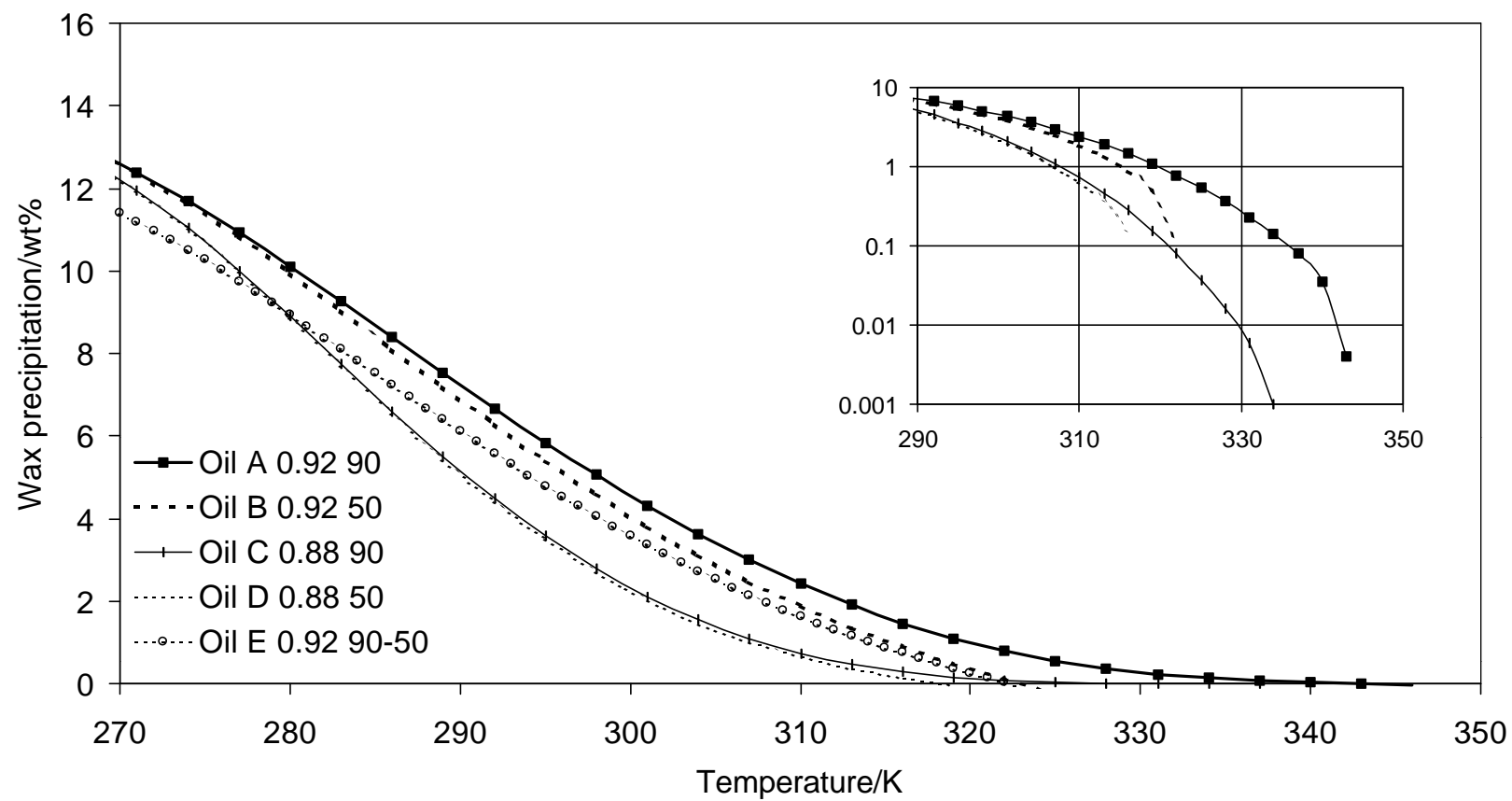
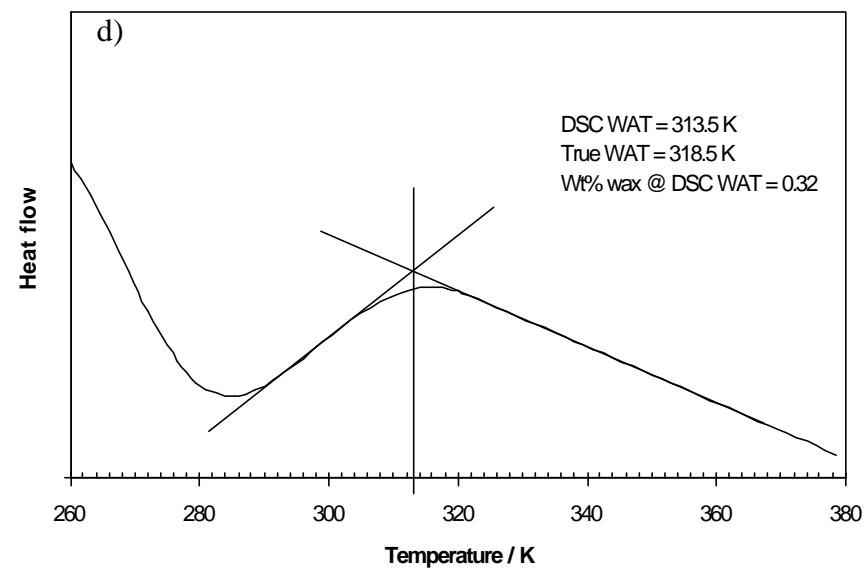
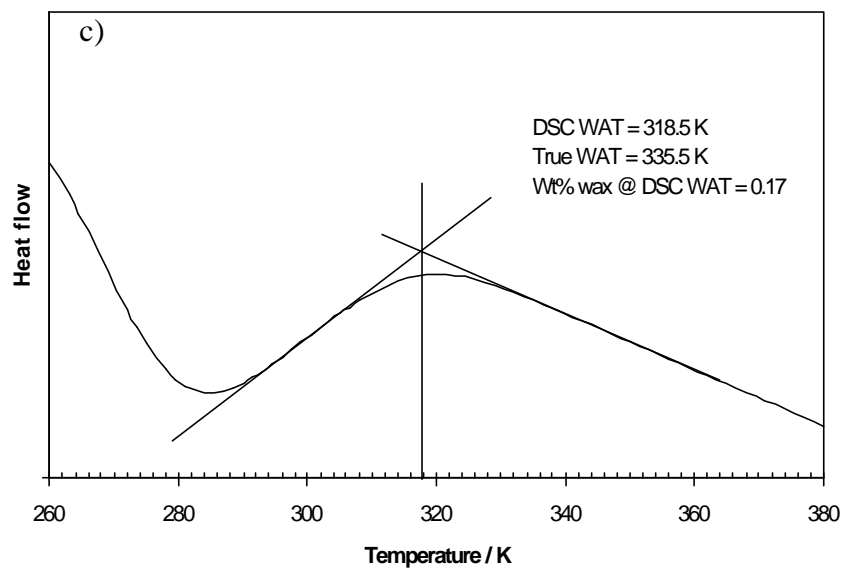
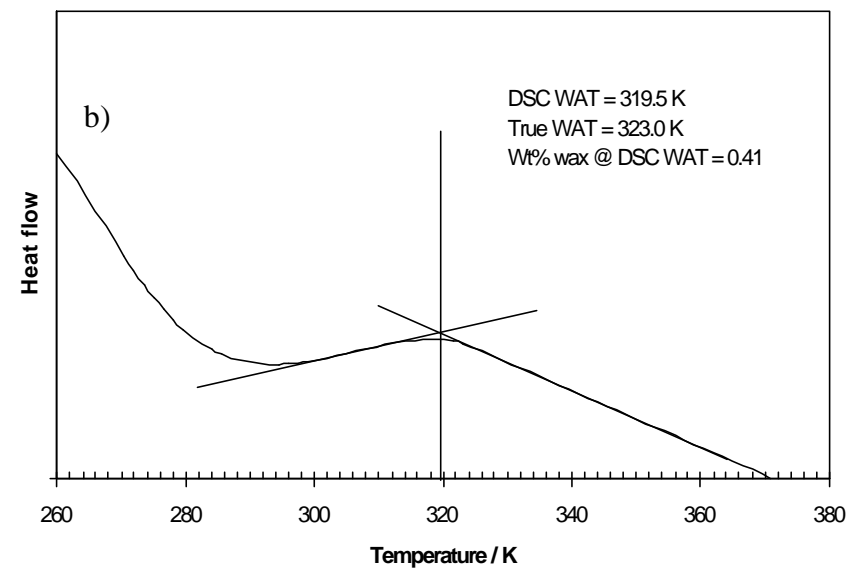
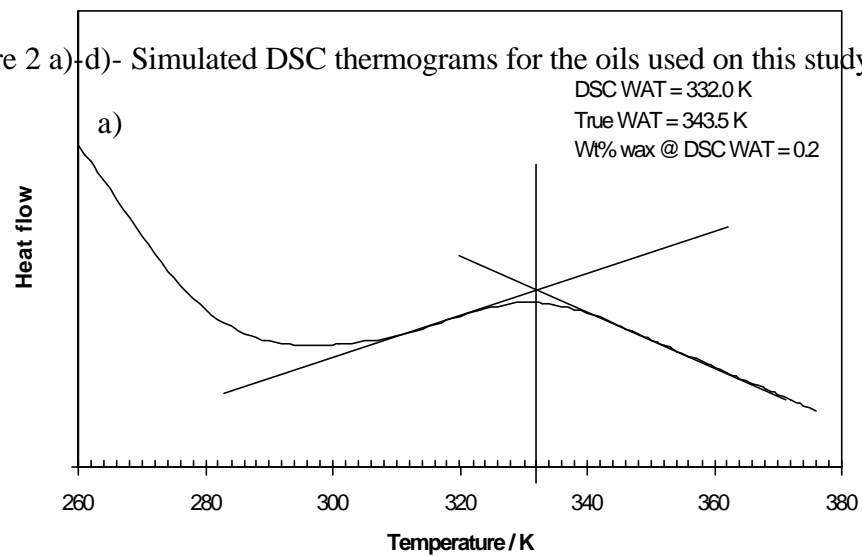


Figure 1- Simulated wax precipitation curves for the oils used in this study. The insert shows the low composition region in semi-logarithmic scale.

Figure 2 a)-d)- Simulated DSC thermograms for the oils used on this study.



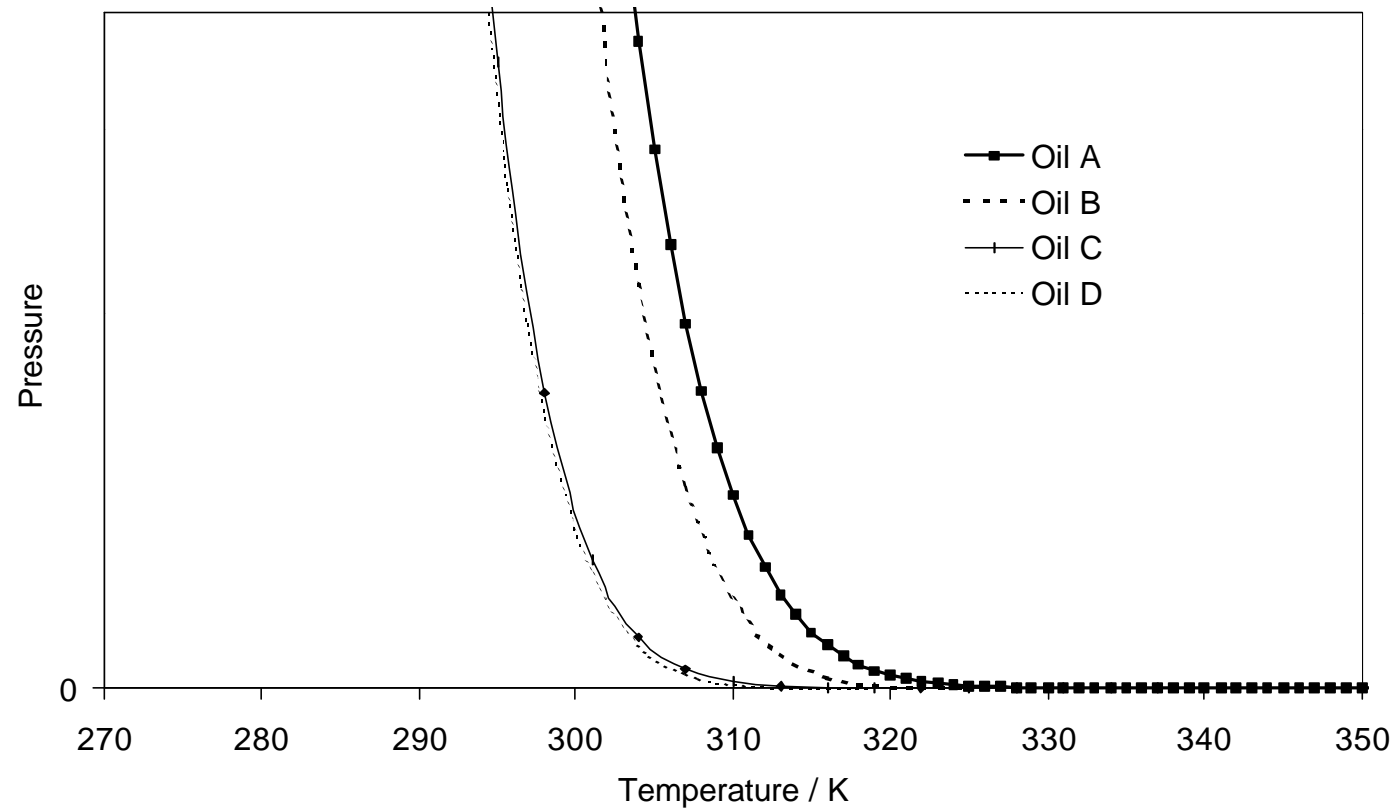


Figure 3- Pressure drop across a filter plugged by the oils used in this study as function of the temperature.

Figure 4- Dependence on the paraffin decay of the difference between the wax disappearance and appearance temperatures after Rønningsen et al. (1991).

