DETERMINATION OF CRYSTALLIZATION OF WAXY CRUDE AND THE INFLUENCE OF DILUENTS

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ABSTRACT

This paper discusses the determination of crude oils behaviour with high wax content. The crude oil begins to behave as pseudo-plastic fluid at temperature 10°C above its onset crystallization temperature (WAT). This is the temperature that characterizes the waxing potential of crude oils. In this study, laboratory tests that are used to determine the cloud point and quantify the deposition of paraffin wax were investigated. The influence of petroleum-based diluents on the onset crystallization point have also been studied. Two waxy crude samples from PM8 oilfields were used in this study. Accurate measurement of WAT will help to determine the optimum operational condition without facing the wax problem. Application of diluent to reduce the wax formation is restricted to only low wax content of crude oil.

1.0 INTRODUCTION

Paraffin constituent of most crude oils. It is well-recognized production problem which is related to the deposition of solids paraffin in downhole tubulars, surface equipments and pipeline. The formation of paraffin solids of which usually called wax is actually an example of fluid/solid phase equilibrium. It could be explained in term of established principles of thermodynamics of solution i.e. the solution of higher-molecular-weight hydrocarbons in lower-molecular-weight hydrocarbons that act as a solvent. In other words, high-molecular-weight solids precipitate whenever anything occurs that decreases the carrying capacity of the solvent.

The flow of crude oil in gathering system and trunkline depend on fluid properties, shear stress of flow, pumping pressure and operating temperature. But in most cases temperature is the main parameter that controls the deposition of wax. So it is important to measure the temperature dependant properties that characterize the waxing potential of crude oil. This paper will first discuss inadequacies of experimental cloud point methods to field occurance of paraffin wax. Second, the paper will discuss the application of diluent in reducing the tendency of wax formation.

2.0 CLASSIFICATION OF ANALYSES

Cloud point has been used as a reference in many years to determine the paraffin wax deposition. As long as operating temperature remain above the cloud point, wax deposition will not occur. According to Reistle[1], the deposition of crude wax, is commonly known as paraffin wax in the flow lines, consists of very small wax crystals that tend to agglomerate and form granular particles of wax about the size of grains of ordinary table salt. Therefore, it is very important to determine the lowest temperature of which the bulk of fluid reach the cloudy condition. This measured temperature is called cloud point classified by ASTM D2500-88 or IP 219/82. However these methods could only be applied for clear fluids since they rely on visual observation of the wax crystals[2]. For most crude oils cloud point cannot be determined directly from the standard procedure. A term called 'Wax Appearance Temperature' (WAT) is introduced by many researchers to represent the ASTM cloud point.

A technique called Differential Scanning Calorimetry (DSC) is introduced as a standard method to determine the appearance of the first crystal from the crude oil. The technique involves the recording of the energy change in the thermodynamic phase transformation at isobaric condition. Figure 1 shows a typical result of Differential Scanning Calorimetry method. A viscometry method[3] is also capable to estimate the cloud point of the crude oil by plotting of viscosity versus reciprocal temperature as shown in Figure 2. Typically the cloud point would be taken as the temperature where the data begins to deviate from linearity. At the point of deviation, sufficient wax has crystallized to change the rheology of the crude oil from Newtonian to Non-Newtonian[4]. This condition shows that the viscosity of crude oil becomes dependant upon the shear rate.

Another popular technique that being used widely in the industry is by visually determine the temperature at which first paraffin begins to crystallize in the oil. The sample is preheated and transfered to a microscopic slide and covered with a cover slip. The sample is viewed under polarized light so that only crystallize material (wax) is visible.

Table 1 and Table 2 report the comparison of cloud points obtained via various methods. In almost all cases, it has been found that the micriscopic cloud point is higher than the cloud points by DSC and viscometry methods. The microscopic cloud point represents the highest temperature at which wax crystallization and deposition begin to occur. It is also found that measurement from DSC and viscometry methods are lower than the true cloud point. The reason is associated to the condition where the first crystal will be formed once the crude oil reaches the cloudy condition. Sometimes the crystallization point is very close to the cloud point because the crystallization process is accelarated by the present of external nuclei such as sand, resin and other impurities in the crude oil. Thus, DSC method is used to study the waxing potential of two crude oils in pipeline operations.

3.0 FIELDSTUDY

There are many newly developed oilfields producing crude oils which contain a considerable amount of wax. It is expected that the downhole tubulars, flowlines, separators and pipelines need frequent maintenance and cleaning to avoid the deposition of wax. The maintenance of these equipments are very costly and the flow of crude oil has to be stopped. Optimum operational conditions are determined from the cloud point or wax appearance temperature. Both parameters must be measured precisely and methods must be analyzed in order to reduce the the risk of wax problem.

Two crude oils were used to study the waxing potential. Samples were taken from the exploration fields, Penara and Larut. The wax content of Penara and Larut were about 25% and 15% respectively. The study was conducted by using Seiko SSC5200 Differential Scanning Calorimeter and the cooling chamber was modified with refrigerated bath to control the cooling rate.

Samples were heated up to well above the wax appearance temperature and were then lowered to any desired values. Both crude samples were seen in solid form at the ambient conditions. Prior to the measurement, samples must be homogeneized to ensure that solid crude oil was melted to liquid form. To perform such test, samples to be analyzed were maintained at 55°C initially for at least one day and carefully stirred before the start-up of the experiment in order to avoid recrystallization and further deposits. The cooling rate used in the study was 5°C/min for the temperature of 10°C above the expected wax appearance temperature (WAT) and between 0.5°C/min and 0.1°C/min for the temperature range close to WAT. Samples were diluted with three light hydrocarbon liquids i.e. Semangkok crude oil, kerosene and gasoline. The purpose of dilution anaylsis was to study the effect on WAT and suitability of the method to reduce the risk of waxing and deposition in the pipeline.

The reference cell in the DSC Chamber is generally empty. The hot samples were introduced into the test cells, sealed and maintained at 80°C for 1 hour to prevent futher possible leaking. Once the two cells have been introduced in the calorimeter, the temperature of the oven was decreased linearly via the selected cooling rate.

4.0 RESULTS

All samples we have tested are presented in Table 3. The result shows that none of samples were failed to crystallize using selected cooling rate. The wax crystallization onset temperature is then determined from the enthalpy curve recording. The WAT varies depending upon the crude and quantity of diluents. For undiluted Penara sample, the WAT and enthalpy of crystallization are 47.05°C and 86.3 mJ/mg respectively. Figure 3 and Figure 4 represent the DSC curve and enthalpy change for both crude oil samples. Penara crude shows an early crystallization called 'wiggle' due to high temperature crystallization which was occured prior to reaching the actual WAT. The influence of diluents (or light hydrocarbon liquids) on the onset crystallization have been studied. It can be seen that variation of the WAT is almost depends on quality of sample. Crude oil which contains of higher percent of wax is difficult to be treated with diluents. However gasoline is a good candidate to reduce the WAT of crude oil but is not economical if the concentration is greater than 30%. Figure 5 shows the effect of diluents on WAT. The dotted horizontal line indicates the typical seabed temperature for the South China Sea. It is found that treatment by using this technique is able to alter the WAT provided that the concentration of gasoline is greater than 15% in weight. Larut crude is expected to flow at any designated pressure and flowrate without facing any crystallization and deposition problems in pipelines as long as the modified WAT is lower than the seabed temperature. However, this technique failed to modify the WAT of Penara even at higher concentrations. Although kerosene and gasoline are recoverable but the consumption is not economical. Therefore the technique is not applicable for Penara crude oil. The results of heat capacity and enthalpy are reported in Table 4.

5.0 CONCLUSION

In the work presented above, the salient points are:

- The most suitable laboratory technique will be able to determine accurate cloud point and wax appearance temperature. This is the most important tool in predicting the waxing potential of any crude oils.

- Two waxy crude oils have been analysed and measured WAT is used as criteria to determine the operational conditions. Early crystallization was detected for Penara crude by Differential Scanning Calorimeter.

- Diluting of crude oil with light hydrocarbon may reduce the wax formation temperature about 5-10^{o}C. The change of WAT depends on amount of paraffin wax in the crude oil.

ACKNOWLEDGEMENT

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Table 1 : Comparison of WAT measurement techniques

Method	Advantages	Disadvantages	Comments
Visual (ASTM)	Quick, cheap	Not reproducible, no good for dark fluids	Not to be relied on
Viscosity	Can be adapted for high pressures	Not good for low wax content oils, Interpretation of results	Limited application
Blocked filters	Can be adapted for high pressures, simple equipment	Interference from other solids	Most common method for live systems. Requires good sample preparation
Polar Microscope	Sensitive, easy interpretation	Difficult to adapt for use at high pressures, results depend on cooling rate	Popular method with good sensitivity. becoming standardised
DSC	Standard equipment, can also provide wax content	Trade off between sensitivity and accuracy, Difficult for low wax oils	Popular method, but can give low readings
Density change	Can be used at high pressures	Specialist equipment, not widely available, interference from other solids	Not widely used at present

Table 2. : Comparison of cloud point and WAT result of six different crude oils.

OIL	DSC (5°C/MIN) (°F)	VISCOSITY (°F)	MICROSCOPE (°F)
1	79	77	98
2	92	86	100
3	88	99	137
4	77	81	97
5	120	122	134
6	53	ND	100

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Figure 1 : A typical DSC curve

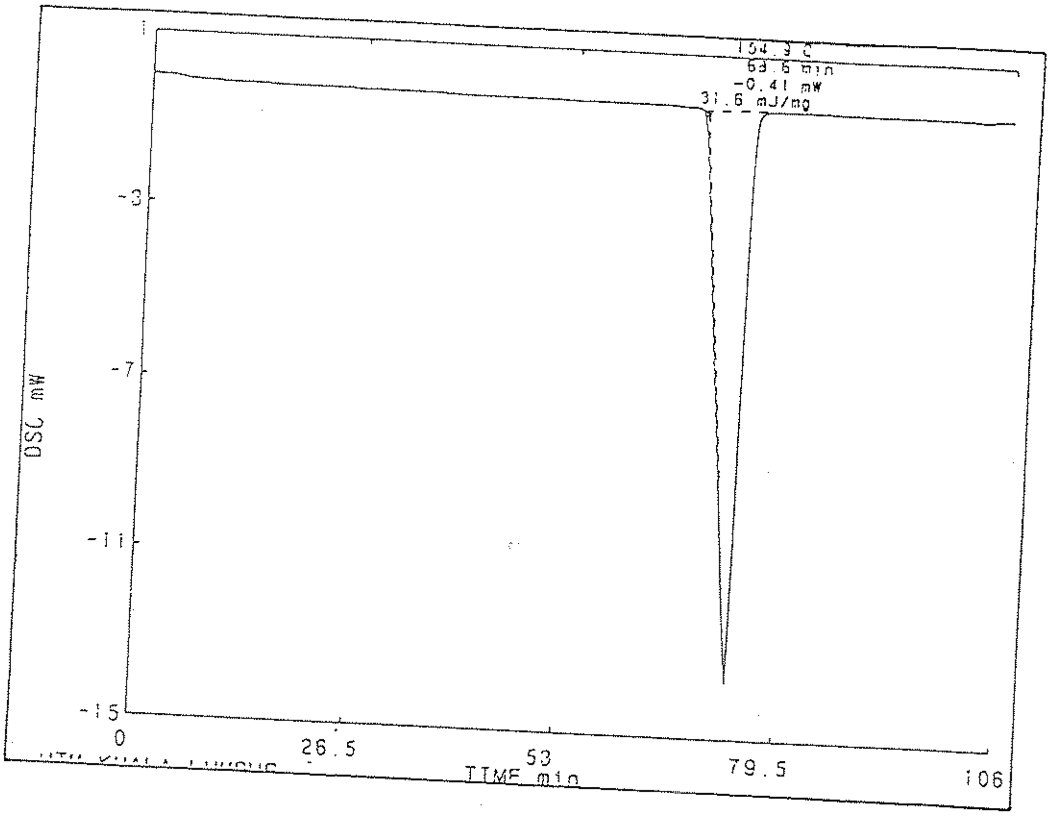

Figure 2 : Rheological Changes AT Cloud Point Dead Crude, 45-4°C, 100 s^{-1}

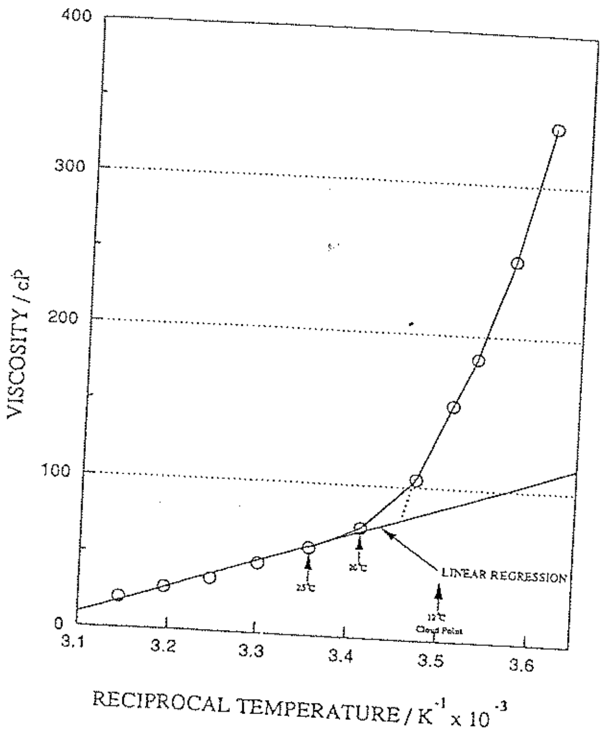

Table 3 : Result of WAT and Effect of Diluents

PERCENT OF DILUENTS	WAT(°C) PENARA CRUDE OIL		
	SEMANGKOK	KEROSENE	GASOLINE
0	47.05	47.05	47.05
10	45.86	45.05	44.43
20	44.25	42.53	42.15
30	42.22	40.55	38.87
40	41.14	37.65	36.41
50	38.78	33.23	32.62
60	36.63	32.10	29.46
PERCENT OF DILUENTS	WAT(°C) LARUT CRUDE OIL		
	SEMANGKOK	KEROSENE	GASOLINE
0	35.67	35.67	35.67
10	35.58	33.82	32.18
20	34.99	32.87	31.32
30	33.57	31.71	30.60
40	32.11	29.87	28.65
50	31.27	27.79	26.52
60	30.70	27.66	25.34

Figure 3a : Dsc Curve for Penara Crude Oil

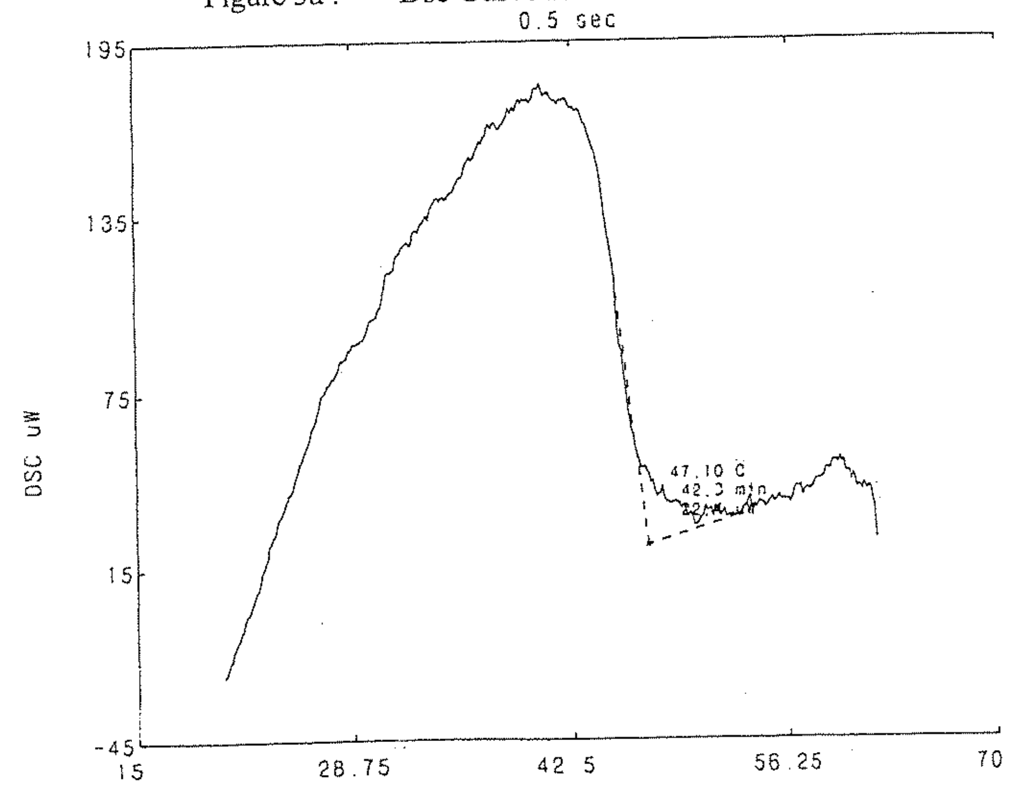

Figure 3b : DSC Curve for Larut Crude Oil

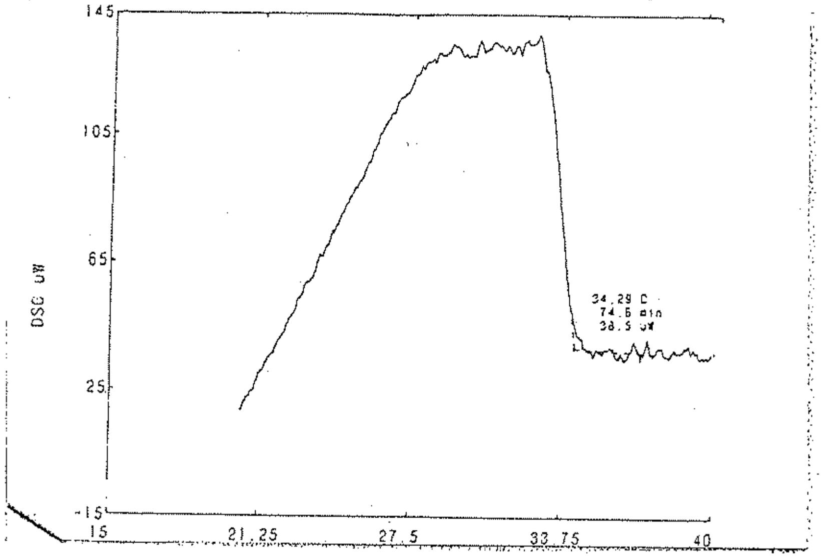

Figure 4a : Determination of Enthalpy Change of Penara Crude Oil

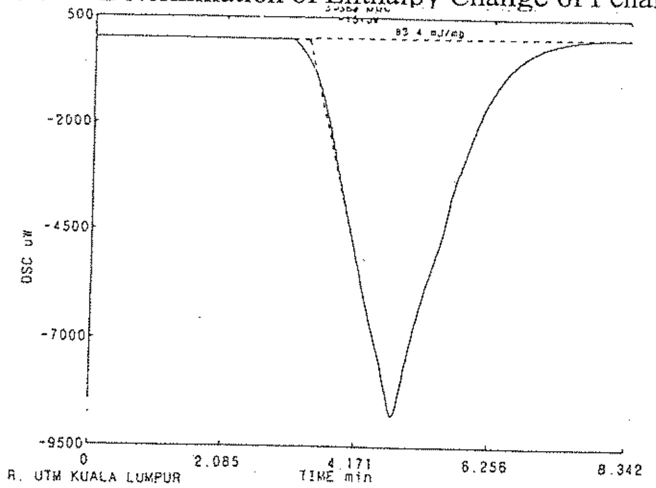

Figure 4b : Determination of Enthalpy Change of Larut Crude Oil

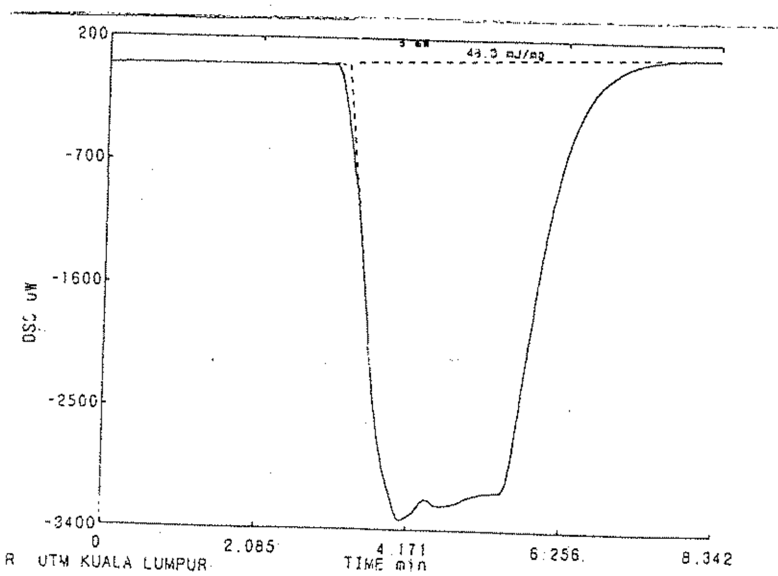

Figure 5 : The effect of diluents on WAT