Characterization of Paraffinic Composition in Crude Oils

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ABSTRACT

One of the significant risks in flow assurance management would be the deposition and gelation of paraffin waxy in crude oils transportation. This is highly influenced by the structure of hydrocarbons in the produced composition from the well. In this paper, investigations on the behaviour of waxy crudes, especially in Malaysian oil basins, were carried out. The study focuses on the carbon number distribution, wax appearance temperature (WAT) and wax content of four crude oil samples from different field locations (named as sample-1, …, sample-4). Results show that crude oil samples with higher mol. percentage of carbon distribution, from C_{20} to C_{40}, (paraffinic composition) contains higher wt% wax content, and subsequently resulting in higher wax appearance temperature. Further similar investigations on other field locations will assist in characterising the paraffinic composition in Malaysian oil basins.

Keywords- Carbon number distribution, Crude oil, DSC, Gas chromatography, Mass spectrometry, Paraffinic distribution, Wax appearance temperature, Wax content.

INTRODUCTION

The economic viability of all offshore projects has always been the main concern of all parties and it is highly dependable on realistic estimations of flow problems as well as associated remedial and preventive techniques. In Malaysia, one of the identified problems concerning the flow assurance studies would be the wax deposition in the crude oil pipeline systems. Wax deposition occurs as crude oil generally has n-paraffins as constituents; when the wellbore temperature falls below the wax appearance temperature (WAT), wax crystallization forms and contributes to increase in pressure drop, reduction in productivity and subsequently choking the production lines, causing emergency shutdown.

Crude oils in Malaysia have been found to contain significant quantities of wax where those with high paraffin and pour point are generally classified as waxy crude. In subsea completion (where flowlines on the ocean floor ranges about 1.5°C to 5°C), each wax component becomes less soluble until the higher molecular weight components solidify. The onset crystallization is known as the cloud point or WAT. As the waxy crudes continue to cool to the temperature below WAT, the crude's flow properties change from a simple Newtonian fluid to a two-phase dispersion non-Newtonian fluid. This results in gelation of crudes and loss in flow-ability.

Currently, a few preventive and curative methods have been developed to handle flow assurance risks imposed by waxy crudes, which fall under three major categories: thermal, mechanical and chemical. However, all the methods have certain disadvantages and tend to increase the operating expenses (Ewkeribe, 2008). Furthermore, the production problems and developed solutions vary from reservoir to reservoir due to difference in paraffinic characteristics and contents.

As methods that are proven to be effective in certain system do not guarantee success in problem solving of other reservoirs or even in various wells within the same reservoir, it is essential to study and characterize the paraffin in crudes, specifically, in order to counter the wax deposition in wells. Therefore, this paper aims to study and characterize the behaviour of some Malaysian crudes, through experimental measurement to further determine and analyze the carbon number distribution, WAT and wax content. Due to the confidentiality restrictions as needed by the client, the samples will be denoted as sample1, sample2, sample3, and sample4. The study is carried out in two major phases: experimental measurement as well as analytical prediction.

ANALYSIS OF WAXY CRUDES

Despite the compositional complexity, most crude oils behave as simple Newtonian liquids at high temperature, typically above 40°C. At this point, crude oils have certain viscosity at the given temperature. The viscosity of the crude oils can also be predicted accurately through corresponding states models or correlations in measurable physical properties such as density (Pedersen and Ronningsen, 1999). However, as the temperature reaches the WAT, wax precipitation occurs, causing an increase in viscosity and pressure drop in pipelines. When the concentration of wax particles is sufficiently high, the flow properties of the crude oil will gradually change from Newtonian to non-Newtonian behaviour. According to Lee (2003), the transition takes place at the temperature about 10°C to 15°C below the WAT and corresponds with a solid wax fraction of 1 to 2 wt%. As the temperature approaches the pour point, the crude oils exhibit a gel-like form which is of highly non-Newtonian behaviour. The weight percent of solid wax reaches about 4 to 5% at this point. The properties of crude oils are unpredictable in the state of non-Newtonian behaviour.

Carbon number distribution

Generally, crude oils contain mixture of light and heavy hydrocarbons that can be classified as paraffins, napthenes and aromatics. The lighter parts of the crude oils keep the heavier parts (wax and asphaltene) in solution. The presence of light ends increases the solubility of wax in crude oils, besides depending on pressure, temperature and composition of crude oils.

The paraffin in crude oil is of those normal hydrocarbons with high carbon number. Normal hydrocarbons that composed of more than 16 carbons are called “wax”, (Biao and Lijian, 1995). The wax in crude oils is a mixture of normal hydrocarbons with different carbon number distributions. Describing the hydrocarbon composition of the wax in crude, Kok and Saracoglu, 2000 stated that there are two types of wax which are commonly found in crude oils; macrocrystalline wax (from C_{18} to C_{36}) and microcrystalline wax (from C_{30} to C_{60}) which both are made up of aligned paraffinic and napthenic molecules,. Paraffin waxes are also known as macrocrystalline waxes which composed of mainly straight-chain paraffins (n-alkanes) with varying chain length; whereas, microcrystalline or amorphous waxes contains high portion of isoparaffins (cycloalkanes) and napthenes, (Elsharkawy *et al*. 1999). The presence of these solid particles causes the change of flow behaviour from Newtonian to non-Newtonian, especially paraffin waxes which respond easily to changes in temperature due to its straight-chain structure.

To design pipelines and to handle the facilities for waxy crude oils, it is important to know the amount of wax that will precipitate when the crude oil is exposed to the lowest temperature. By having carbon number distributions and sub-classifications of wax at different temperature plus Differential Scanning Calorimetry (DSC) data, solid fluid phase behaviour can be modelled and correlated using various methods, including specifically-modified versions of Hildebrand’s

Regular Solution Theory (Carnahan 2007). Analyses for the precipitated wax also reveal a quasi-rectilinear correlation between log mass percentage wax and carbon number, Peters *et al*, 1988. Modern calculations method which based on principles of thermodynamics of solutions also can accurately describe the solution behaviour of waxes in crude oils.

Thermal analysis

Data obtained from DSC illustrate the exothermic process (cooling) and the endothermic process (heating), the onset crystallization temperature (also known as WAT) and the dissolution temperature. The plot also would reveal two characteristic peaks: liquid-solid transition and solid-solid crystalline. From the DSC thermal analysis data, the wax content can be identified through analysis method developed by Chen *et al*. 2003. The wax content of the crude oil is proposed and proved to be the Q (total thermal effect of wax precipitation) ratio of crude oil and its corresponding wax obtained by using standard acetone method, i.e. Q_{oil}/Q_{wax}. The proposed method is proved to be in good agreement with those determined by standard acetone method, with an absolute average deviation of 0.82 wt% (Chen *et al*., 2003).

To determine the wax content by using DSC, base-line computation and the knowledge of experimental equation $\Delta H_{diss} = f(T)$ are required. The base-line for crude oil is generally assumed to be: (1) a line between the end of the exothermal effect after the glass transition temperature and the end of the dissolution of wax, or (2) a straight line computed by least-squares fitting with the values of calorimetric signal included the temperature range from wax appearance temperature range from WAT to 10K above (Ewkeribe 2008).

According to the method proposed by Chen *et al*. 2003, wax content of crude oil can be determined by using total thermal effect Q ratio of the crude oil and the corresponding wax sample obtained by standard acetone method. The total thermal effect Q of wax precipitation can be computed by integrating the area between DSC calorimetric signal curve and the line connecting the two temperature signals. Empirical correlations also have been established, where:

- The linear relation between the Q_{oil} and the corresponding wax contents determined by Q_{oil}/Q_{wax} method can be expressed with a correlation coefficient of $R^2 = 0.9837$

$$c_{wax} = 0.75Q_{oil} + 0.20 \qquad (1)$$

- The linear relationship between the Q_{oil} and the corresponding wax contents determined by the standard acetone method can be expressed with a correlation coefficient of $R^2 = 0.9651$

$$c_{wax} = 0.73Q_{oil} + 0.74 \qquad (2)$$

The established correlations provide a new method to improve the accuracy of computing the amount of precipitated wax in crude oils at different temperature.

EXPERIMENTAL METHODOLOGY

Successful experimental tests of crudes, using standard equipment requires proper sample preparation. Accordingly, the preparation procedure is detailed in this paper. Descriptions of the used equipment and measurement procedures are also included in the paper

Preparation of samples

A total of four crude oil samples have been received from different production fields in Malaysia, named as sample1 to sample4.

As the samples come in bulk volume (around 4L to 5L), the samples were firstly heated to 80°C for 8 hours in water bath to eliminate the thermal history as well as to avoid separation of heavy crudes and light crudes, as recommended by Wikipedia – Gas Chromatography Mass Spectrometry. (Retrieved on March 10, 2012).

Throughout the heating process, the samples were stirred from time to time to ensure complete dissolution and homogeneity. The samples were then transferred to small-sized containers while the temperature is still relatively high. The preparation work done helps to shorten the heating process prior to future experimental measurements as smaller volume is involved. Only an average of 1 hour to 2 hours was required for pre-heating before the commencement of future experimental measurements.

Gas Chromatography Mass Spectrometry (GCMS)

In this project, GCMS is used as it combines the features of gas-liquid chromatography and mass spectrometry to identify different substance within a test sample which is the carbon number distribution in the crude oil samples. By using GCMS, a much finer degree of substance identification is allowed than when either unit is used separately. This is because the mass spectrometry process requires very pure samples while gas chromatography uses traditional detector. Combining the two processes reduces the possibility of error as it is extremely unlikely for two different molecules to behave in the same way in two different processes.

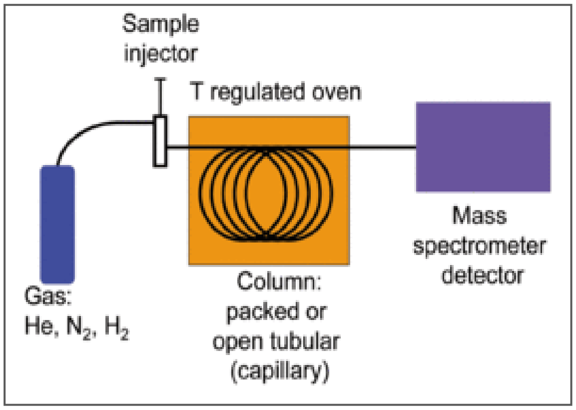

Fig. 1: Schematic Diagram of A GCMS [Wikipedia]

Fig. 2: Shimadzu 5050 GC Coupled with Shidmadzu 5973 with Mass Selective Detector

GCMS used for the experimental measurement is Shimadzu 5050 GC coupled with Shimadzu 5973 with mass selective detector. The chosen column for the experiment is DB-5 capillary column with length of 30 meters, inner diameter of 0.32 millimetres and phase thickness of 0.25 millimetres. The procedure of the experiment was commenced by setting the temperature to be 120°C hold for 3 minutes until it reached maximum temperature of 270°C and hold for 40 minutes. Temperature increasing rate was set to be 10°C/min. At the temperature of 300°C, splitless injection was carried out with constant flow rate of 2cm^3/min. The Mass Spectrometry (MS) transfer line was set at 300°C and the ion source was kept at 230°C. The same procedure was applied for the four samples of crudes.

Differential Scanning Calorimetry (DSC)

When heated and cooled at specific cooling rate, DSC measures the difference in absorbed or released heat between two samples, which are the reference and the test sample. The reference material used has identified properties and was thermally inert over the specified temperature range. Due to the release of the crystallization heat, the test sample at WAT cools slower than the reference. Changes are captured by the analyzer in order to compute the difference in required heat input to maintain the temperature of both reference and test sample equally. If a sample's enthalpy of fusion is known, the weight fraction of crystallized wax also can be calculated. Solid weight as a function of temperature defines the solubility curve for the past sample.

Fig. 3.a: Differential Scanning Calorimetry

Prior to thermal analysis using DSC, Thermal Gravimetric Analyzer (TGA) was carried out to investigate the changes in weight in relation to temperature change. A derivative weight loss curve can identify the point where weight loss is the most apparent. The boiling point can also be determined as TGA is acting of heat which is high enough to temperature for the components to decompose into the gas, where it is dissociates into air. Hence, the maximum heating temperature of DSC should be set lower than the boiling point to prevent vaporization of the crude oil samples. Simultaneous TGA-DSC helps to measure heat flow and weight changes in a sample as a function of temperature. The complementary information obtained allows differentiation between endothermic and exothermic events with no associated weight loss, such as melting and crystallization.

Fig. 3.b Thermal Gravimetric Analyzer (TGA)

RESULT AND DISCUSSION

Carbon number distribution

From the GCMS, the experimental measurements are shown in the form of chromatogram where the peaks represent the types of component present in the compound of the crude, as shown in Fig. 4, for sample-1.

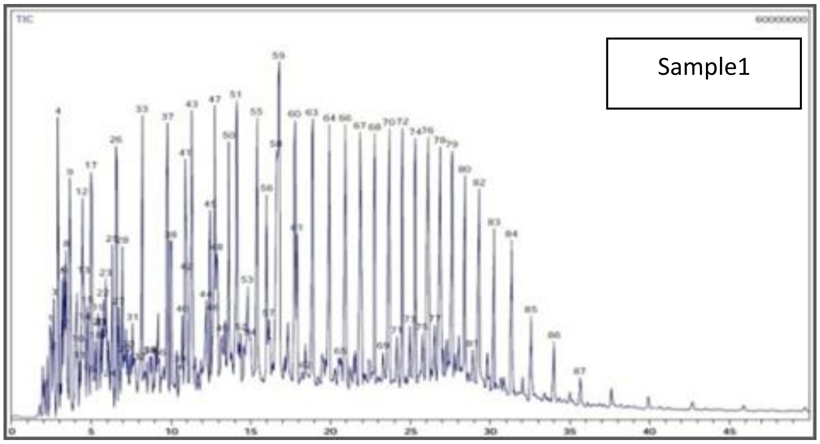

Fig. 4: Sample of Chromatogram from GCMS

The X-axis of the chromatogram represents the retention time (which is the time/period required for each compound to elute), while the Y-axis represents the absorbance. The lighter components are more towards the right of the chromatogram. The retention time, types of components and concentrations can be obtained from the GCMS experimental measurements.

In this study, the presence of carbon number from C_{20} to C_{40} is focused, where the straight-chain paraffins (n-alkanes) are mainly found. Results of Mol Percent vs Carbon Number distributions for each sample are plotted and shown in Fig. 5, 6, 7, and 8, for Sample-1, Sample-2, Sample-3, and Sample-4, respectively.

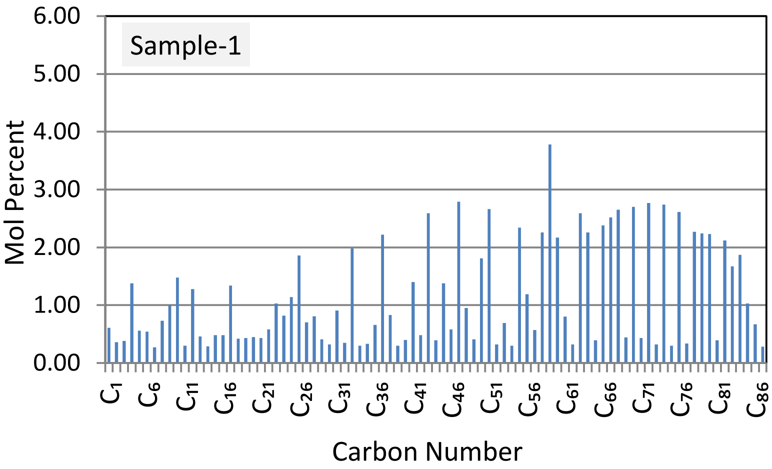

Fig. 5: Measured Mol Percent vs Carbon Number of crude sample-1

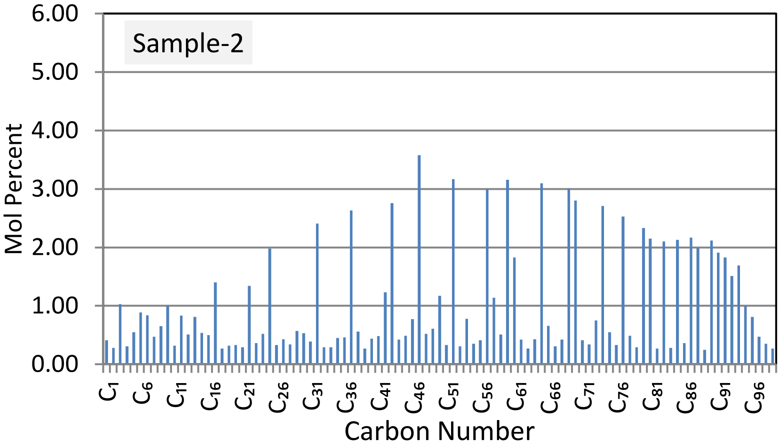

Fig. 6: Measured Mol Percent Vs Carbon Number of crude Sample-2

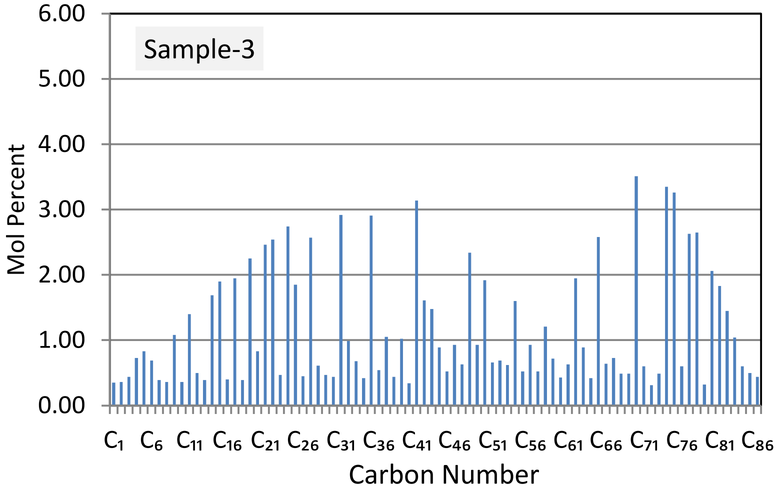

Fig. 7: Measured Mol Percent Vs Carbon Number of crude Sample-3

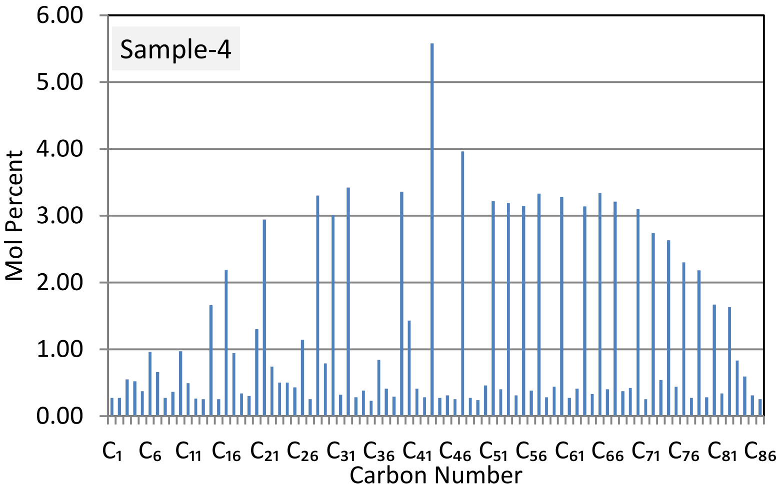

Fig. 8: Measured Mol Percent Vs Carbon Number of crude Sample-4

Data of Cumulative Mol Percent (from C_{20} to C_{40}) for the four crude oil samples are shown as below.

TABLE I. Table of Cumulative Mol Percent from (C_{20} to C_{40}) for Each Sample

Samples	S-1	S-2	S-3	S-4
Cumulative Mol Percent (from C_{20} to C_{40})	16.83	15.21	26.74	25.86

Crude oil samples from field location 3 and 4 have higher percentage of paraffin wax compared to crude oil samples from field location 1 and 2. This will also directly affect the WAT as paraffin waxes react and respond easily to temperature changes due to the straight chain structure. The higher the mol percent of paraffin wax in a crude oil sample, the higher the WAT will be as the wax content of the crude oil samples will be indirectly affected and appear higher.

It is obvious that the four samples are compounded of macrocrystalline wax (from C_{18} to C_{36}) and microcrystalline wax (from C_{30} to C_{60}) which both are made up of aligned paraffinic and napthenic molecules, which is same as stated by Kok and Saracoglu, 2000. But in a sense of qualitative analysis, they are compounded of different percentage of carbohydrates. Crude sample-1 contains higher percentage of macrocrystalline wax, while crude samples-3 contains higher percentage of microcrystalline wax. Crudes samples-2 and 4 are showing even distribution of the C_{18} to C_{60}.

Analysis of carbon number distribution also can be determined by simulated distillation (SIMDIS) using both GCMS and supercritical fluid chromatography (SFC). Both methods are within normal experimental scatter but a significantly larger fraction of oil analysis elutes in SFC analysis. Besides, internal standard analysis can be eliminated from SIMDIS without loss of accuracy (Stadler, *et al.*, 1993). There is also no risk of hydrocarbon decomposition at high temperature.

Wax appearance temperature (WAT) and wax content

From the DSC experimental measurement, WAT and wax content of the crude oil samples can be identified. The results are shown as below:

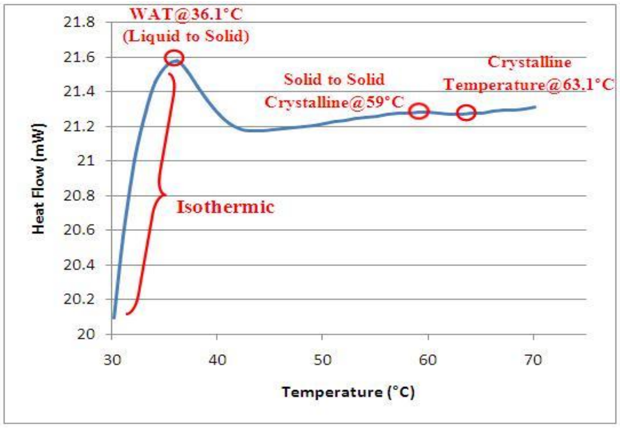

Fig. 9: Heat Flow Vs Temperature measured by the DSC for sample-1.

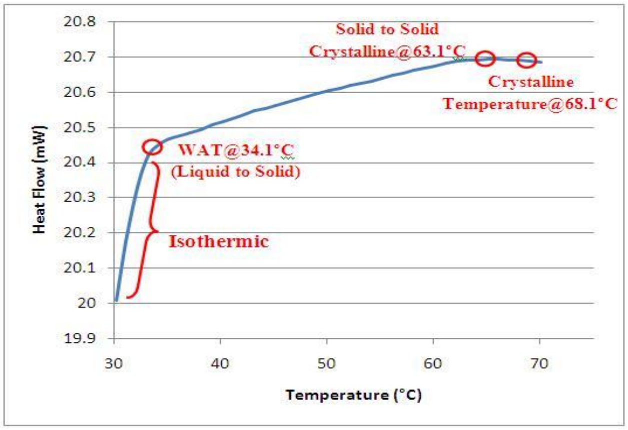

Fig. 10: Heat Flow Vs Temperature measured by the DSC for sample-2.

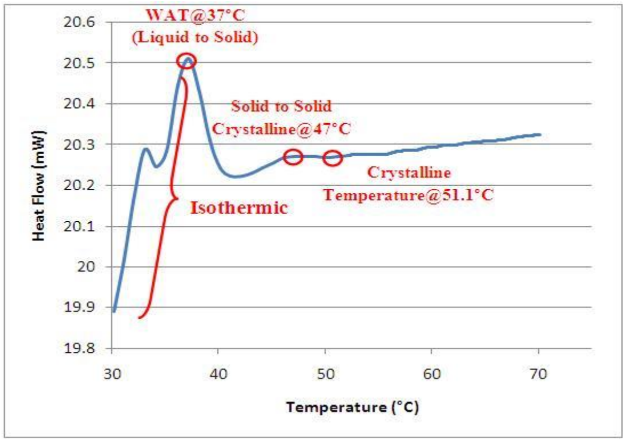

Fig. 11: Heat Flow Vs Temperature measured by the DSC for sample-3.

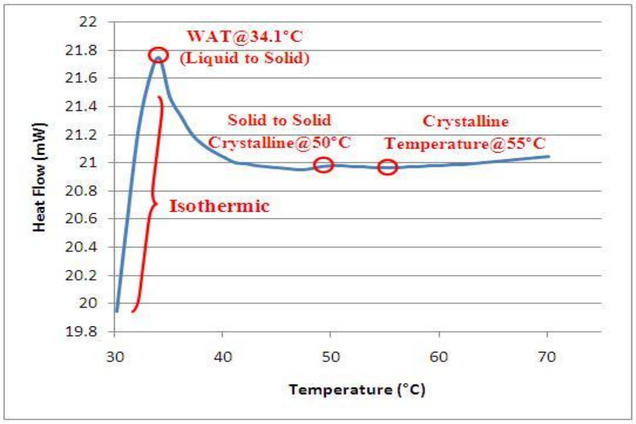

Fig. 12: Heat Flow Vs Temperature measured by the DSC for sample-4

Data of WAT, Solid to Solid Crystalline Temperature and Crystalline Temperature for each sample have been extracted from Fig 9, 10, 11 and 12 and are summarized in table 2.

TABLE 2. Table of WAT, Crystalline Temperature and Crystallization Temperature for Each Sample

Samples	S-1	S-2	S-3	S-4
Wax Appearance Temperature (°C)	36.1	34.1	37	34.1
Solid to Solid Crystalline (°C)	59	63.1	47	50
Crystallization Temperature (°C)	63.1	68.1	51.1	55

Compared to experimental measurement obtained from GCMS, crude oil sample-3 is proven to have the highest WAT. Due to high mol percent of paraffin wax which react easily to temperature changes, crude oil sample-3 also reveal the characteristic of having the lowest crystallization temperature, followed by crude oil sample-4. Meaning to say that crystalline and crystallization temperatures are not following the WAT of the crude. The effective factor on the crystallization is the carbon content and the carbon number distribution in the crude.

From the DSC measured result, the wax content also can be computed through empirical correlations as suggested by Jun Chen *et al*, 2003. Base–line computation is established to determine the total thermal effect Q of the wax precipitation in the crude oil samples.

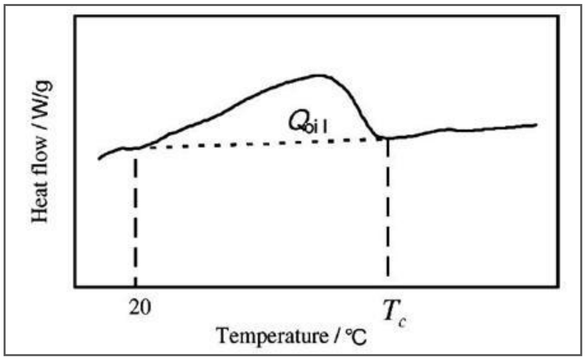

Fig. 13: A Sample of DSC Base-line Computation.

By using the suggested empirical formula, which establishes the relationship between the heat released and the wax content, the prediction of the wax content from the measure of the total heat is allowed. The result of the wax content (wt%) for each sample is shown as below:

TABLE 3. Table of Wax Content for Each Sample

Samples	**S-1**	**S-2**	**S-3**	**S-4**
Wax Content (wt%)	28.90	25.83	33.65	27.35

In order to achieve higher accuracy, more approaches can be utilized for data comparison. For example, to determine the WAT, Cross Polar Microscopy (CPM) and viscometer can be used for data comparison with those generated from DSC (Kelechukwu and Yassin, 2008).

CONCLUSION

From the determined research methodology, data and result from the experimental measurement will be able to indicate the key parameters for the characterization of waxy crudes in Malaysia. The carbon number distributions can be obtained by using GCMS; while, WAT and wax-temperature profile can be obtained from thermal analysis using DSC. Through the DSC base-line computation and empirical correlation suggested by the literature, the wax content of each sample can be calculated.

The characterization of the paraffinic composition in crude oil samples from different four oil fields in Malaysia have been investigated and established in order to assist the prediction of wax precipitation in respective field locations.

The work also can be further expanded and developed to investigate more waxy crude samples from other different field locations in Malaysia to assist in deeper understanding of the crudes' behaviour and subsequently establish the most economical and effective solutions to counter the wax deposition in wells.

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