CERTIFICATION OF APPROVAL

Characterizing the Paraffinic Composition in Malaysian Crudes

By

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Approved by,

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TRONOH, PERAK
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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(WONG NING)

ABSTRACT

Oil companies are now exploring and venturing into the potential opportunities in subsea and deepwater regions which at the same time also increase the risks and technical challenges. However, the flow assurance of reservoir fluids to the surface as well as the subsequent delivery to onshore refinery facilities is still the major concern in justifying the production economics feasibility. One of the significant risks in flow assurance management would be the deposition and gelation of paraffins by waxy crudes.

The current developed methods in handling flow assurance risk imposed by waxy crudes have certain disadvantages and tend to increase the operating expenses. Furthermore, production problems and developed solution vary from reservoir to reservoir.

This project strives to study and analyze the behaviour of waxy crudes especially in Malaysia oil basins. The study focuses on the carbon number distribution, wax content and wax appearance temperature (WAT) that would help to characterize the paraffinic composition in Malaysia's crude oils. In this project, four crude oil samples from different field location (Miri, Angsi, Penara and Dulang) are being emphasized.

A few research methodologies are applied in order to investigate the mentioned properties. The research methodology utilizes certain experimental equipments such as Gas Chromatography Mass Spectrometry (GCMS) and Differential Scanning Calorimetry (DSC). Further analysis and computation on obtained results also is carried out to generate desired research outcomes.

Findings show that crude oil sample with higher mol percent of paraffinic composition has higher wax appearance temperature and wax content, which is obviously observed in crude oil sample from Penara. Hence, there is a linear relationship between the presence of paraffinic composition in crude oil and the occurrence of wax deposition in pipelines.

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ABBREVIATIONS

CPM	Cross Polar Microscopy
DSC	Differential Scanning Calorimetry
GCMS	Gas Chromatography Mass Spectrometry
NMR	Nuclear Magnetic Resonance
PP	Pour Point
UOP	Universal Oil Products
SFC	Supercritical Fluid Chromatography
SIMDIS	Simulated Distillation
TGA	Thermal Gravimetric Analysis (TGA)
WAT	Wax Appearance Temperature

CHAPTER 1

INTRODUCTION

1.1 Background of Studies

For all offshore production, the economic viability of the projects has always been the main concern of all parties and it is highly dependable on realistic estimates 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.

Figure 1.1-Wax Deposition in a Niger Delta Pipelines [1]

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℃ to 5℃), each wax component becomes less soluble until the higher molecular weight components solidify. The onset of crystallization is known as the cloud point or wax appearance temperature (WAT). As the waxy crude continues 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.

1.2 Problem Statement

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 of the methods have certain disadvantages and tend to increase the operating expenses [2]. 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 characterise the paraffin in crudes specifically in order to counter the wax deposition in wells. In this case, an experimental measurement has been carried out on four crude oil samples collected from different field locations, namely Miri, Penara, Angsi and Dulang, in order to further determine the carbon number distribution, wax content and thermal analysis of the crudes.

1.3 Objectives

The main objectives of this project are:

- To experimentally investigate the carbon number distribution, wax content and WAT of crude oil samples from Malaysia's oil basins.
- To study and characterise the behaviour of some Malaysia's crude oils based on experimental measurement.

1.4 Scope of Studies

The project is carried out in two major phases: experimental measurement as well as analysis and computation of obtained results.

The first phase of the project is to investigate the characteristic of paraffinic composition in the crude oil samples. The experimental measurement emphasizes on the following properties: carbon number distribution of paraffin wax (from C_{20} to C_{40}), wax content and WAT. The study of carbon number distribution is conducted through the usage of Gas Chromatography Mass Spectrometer (GCMS); whereas, the wax content and WAT of the crudes are determined through thermal analysis by using Differential Scanning Calorimetry (DSC). A modified standard acetone method, UOP-46 (Universal Oil Products), is applied for dewaxing procedure.

The second phase of the project involves the analysis and computation of obtained result through different approaches. Generated results from GCMS are further processed to establish the graph of mol percent in respect of each carbon number, ranging from C_{20} to C_{40} .The analysis of the carbon number distribution for the precipitated wax is crucial for application of predictive calculation models. For many crude oils, analyses of the precipitated wax reveal a quasi-rectilinear correlation between log (mass percent wax) and carbon number (Peters *et al.*, 1988) [3]. As for the obtained results from DSC, base-line computation is required by establishing a line between the end of the exothermal effect after the glass transition temperature and the end of the dissolution of the wax [4]. To predict the wax content by using the thermal analysis of DSC scan, the method procedure developed by Jun Chen et al is applied where the area between the deflection curve and base-line computation is integrated to study the total thermal heat released of wax crystallization in exothermic process.

1.5 Significance of the Work

Problems associated with wax deposition are generally very costly due to production downtime and removal of wax. Therefore, accurate prediction of WAT and the amount of wax formed at particular condition are extremely important in promoting sustainable operation. However, prior to the establishment of solution, the behaviour and properties of crudes have to be identified and characterised as they vary from reservoirs to reservoirs. This final year project aims to provide the characterisation of paraffinic composition in Malaysia’s crude oils in order to assist future facilities design and management, especially as the country is venturing into deepwater region where temperature is generally very much lower, causing the problem of wax deposition to be more severe.

CHAPTER 2

LITERATURE REVIEW

2.1 Nature of Waxy Crudes

Despite the compositional complexity, most crude oils behave as simple Newtonian liquids at high temperature, typically above 40℃. At this point, crude oils come with certain viscosity at the given temperature. The viscosity of crude oils can also be predicted accurately through corresponding states models or correlations in measurable physical properties such as density [5]. However, as the temperature reaches the wax appearance temperature (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. The transition takes place at the temperature about 10℃ to 15℃ 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 4-5% at this point. The properties of crude oils are unpredictable in the state of non-Newtonian behaviour.

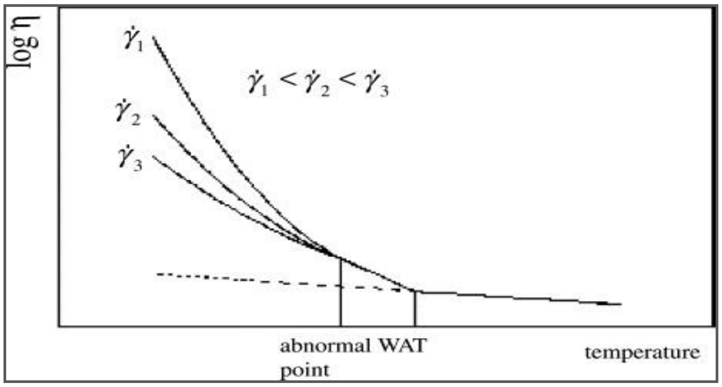


Figure 2.1-Typical Viscosity versus Temperature Chart for Waxy Crudes: Transition from Newtonian to Non-Newtonian Behaviour [6]

2.2 Key Rheological Parameters of Waxy Crudes

2.2.1 Wax Appearance Temperature (WAT)

WAT is the temperature at which the first wax crystals emanate from a clear solution. It also indicates the onset of potential problems while handling waxy crudes. There are various laboratory techniques that can assist in estimating the WAT of waxy crude, such as Differential Scanning Calorimetry (DSC), Cross-Polar Microscopy (CPM), Viscometry and Nuclear Magnetic Resonance (NMR) techniques. However, all the available techniques have not been able to measure the true WAT due to certain volume of wax is required to form for a detectable signal.

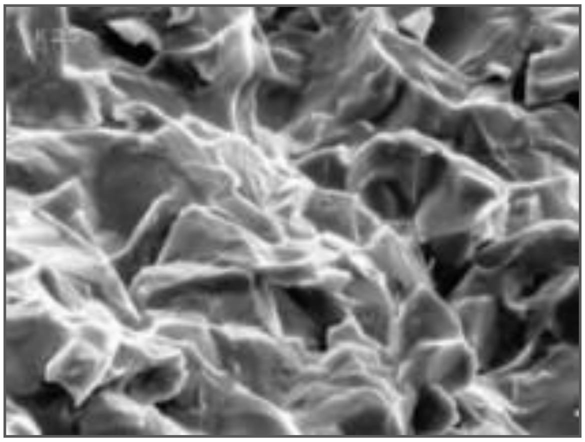


Figure 2.2-Appearance of the Crystals within the Cooled Oil [7]

2.2.2 Wax Content

In petroleum industry terminology, “wax” is defined as any organic solid or sludge phase that appears as a result of decrease in temperature. In petroleum analytical laboratory, “wax” is separated from crude oil samples by cooling to a low temperature and then filtered [3]. Wax fraction quantification in crude oils can be performed through the application of UOP46-85 method [8]. The amount of residue after washing with cold solvent (to remove asphaltic and “non-wax”) is weighed and the wax content of the crude oil samples can be determined through calculation. Determined wax content, in combination with theoretical and empirical calculation methods, is useful data for pipeline design.

2.2.3 Pour Point

Pour Point (PP) temperature refers to the temperature at which the crude oil lost its flow-ability. In another words, it is the lowest temperature where the crude oil stops flowing. It physically represents a balance between gravity forces, such that the viscous effect slightly exceeds the gravitational effect [3]. However, the pour point only indicates that the crude oil is still in fluid form above the PP temperature and high PP is not synonymous with heavy crude oils. A very common method to examine the PP temperature is ASTM D-97. In this method, the oil sample is first heated up and cooled down at specified rate. Then, the flow characteristics are studied at intervals of $3\,℃$. The lowest temperature at which movement of the meniscus is observed is the pour point.

2.3 Wax Analysis

2.3.1 Carbon Number Distribution

Generally, crude oils contain mixture of light and heavy hydrocarbons that can be classified as paraffins, naphthenes and aromatics. The lighter parts of the crude oils keep the heavier parts (wax and asphalthene) 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”. The wax in crude oils is a mixture of normal hydrocarbons with different carbon number distributions which can be indentified by using Gas Chromatography (GC). 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 naphthenic molecules[9]. 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 naphthenes [10]. 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.

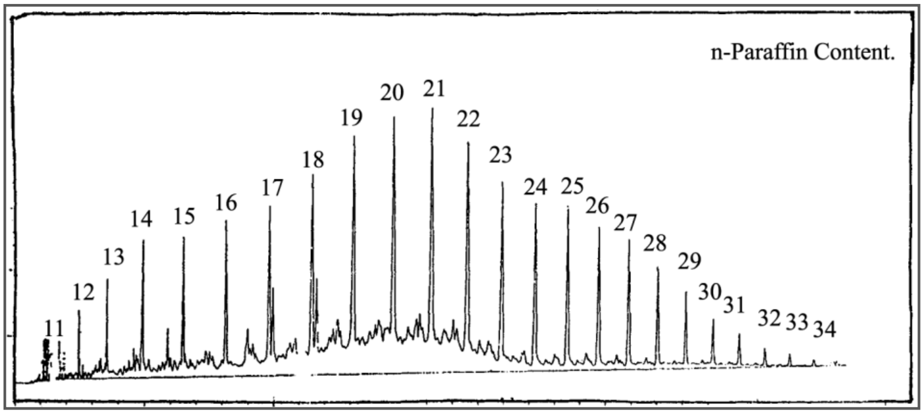


Figure 2.3-Carbon Number Distribution of n-paraffin Fraction Separated from Gas Oil [11]

To design the 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 modeled and correlated using various methods, including specially-modified versions of Hildebrand’s Regular Solution Theory (Carnahan, 1989) [3]. Modern calculation methods which based on principles of thermodynamics of solutions also can accurately describe the solution behaviour of waxes in crude oils.

2.3.2 Thermal Analysis

Data obtained from Differential Scanning Calorimetry (DSC) will illustrate the exothermic process (cooling) and endothermic process (heating), the onset crystallization temperature and the dissolution temperature. The plot also will reveal two characteristic peaks: liquid-solid transition and solid-solid crystalline. From the DSC thermal analysis data, the wax content and Wax Appearance Temperature (WAT) can be identified through analysis method developed by Jun Chen *et al* [4].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%.

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:

- A line between the end of the exothermal effect after the glass transition temperature and the end of the dissolution of wax, or
- 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 [2].

In most cases, the values of calorimetric signal between WAT and 10K above are not straight enough for base-line computation. The glass transition temperature of crude oil is also hard to reach when liquid N_2 cooling is applied. Furthermore, each crude oil comes with a specific experimental equation$\Delta H_{diss} = f(T)$.

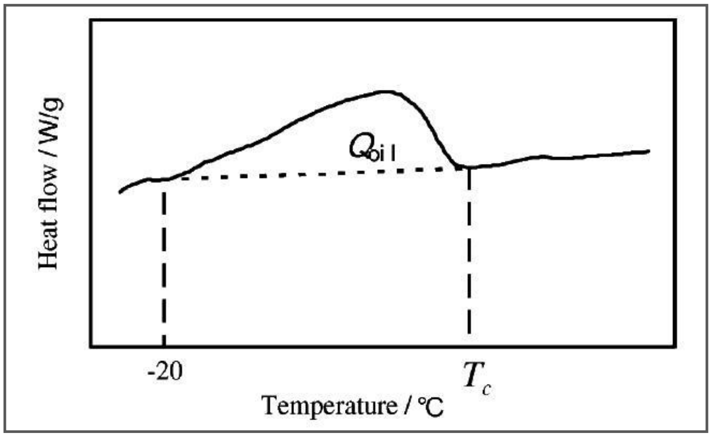


Figure 2.4-A Sample of DSC Curve of Crude Oil [4]

According to proposed method by Jun Chen *et al*, 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 $R^2 = 0.9837$

$$c_{wax} = 0.75Q_{oil} + 0.20$$

- 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 $R^2 = 0.9651$

$$c_{wax} = 0.73Q_{oil} + 0.74$$

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

2.4 Experimental Instrumentation Studies

The working mechanism of various equipment used for the characterisation of crude oil samples is discussed in this section.

2.4.1 Gas Chromatography Mass Spectrometry (GCMS)

A gas chromatograph is a chemical analysis instrument for separating chemicals in a complex sample. A GC separates and analyzes compounds that can be vaporized without decomposition. A flow-through narrow tube (also known as column) with different chemical constituents of sample is installed in GC to enable passing in gas stream at specific rates. When the chemical exits the end of the column, the properties are detected and identified electronically. Interaction with specific column filling (also known as stationary phase) separates different components and allows each one exit the column at a different retention time. Other parameters such as carrier gas flow rate, column length and temperature can be manipulated to adjust the retention time.

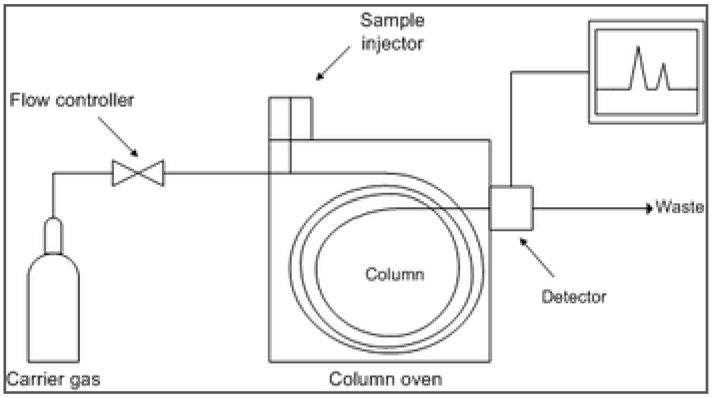


Figure 2.5-Diagram of a Gas Chromatograph [12]

In this project, Gas Chromatography Mass Spectrometry (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. GCMS utilizes a capillary column with specific dimensions (length, diameter, film thickness) and the phase properties that separates the molecules due to the difference in the samples' chemical properties. As the molecules are retained and then eluted from the column at different retention time, mass spectrometer downstream captures, ionizes, accelerates, deflects and detects the ionized molecules separately. The process is done by breaking each molecule into ionized fragments and detected based on the mass to charge ratio.

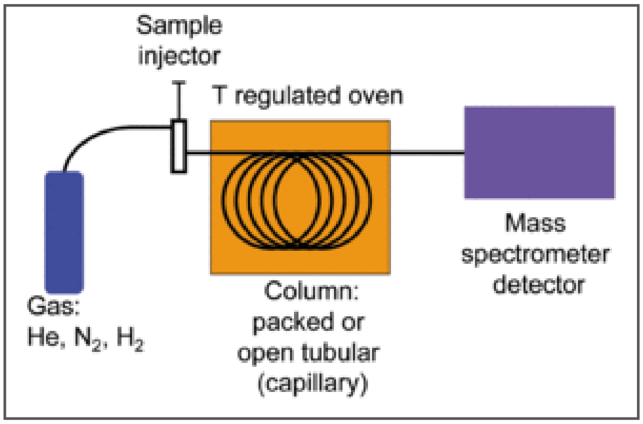


Figure 2.6-Schematic Diagram of Gas Chromatography Mass Spectrometry [13]

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.

2.4.2 Differential Scanning Calorimetry (DSC)

When heated or cooled at specific cooling rate, Differential Scanning Calorimetry (DSC) measures the difference in absorbed or released heat between two samples, which are the reference and the test sample. The reference used for the measurement has identified properties and is thermally inert over the specified temperature range. Due to the release of crystallization heat, the test sample at Wax Appearance Temperature (WAT) cools slower than the reference. Changes are captured by 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 fraction as a function of temperature defines the solubility curve for the test sample [2].

CHAPTER 3
METHODOLOGY

For this project, all the objectives, researches and investigations are achieved through experimental measurements with the aids of several laboratory equipments. The obtained data and information are then further analyzed and computed to reach the desired evaluation outcome in characterising the paraffinic composition in Malaysia's crude oils.

3.1 Research Methodology

3.1.1 Preparation of Samples

A total of four crude oil samples have been received from different field locations, namely: Miri, Penara, Angsi and Dulang.

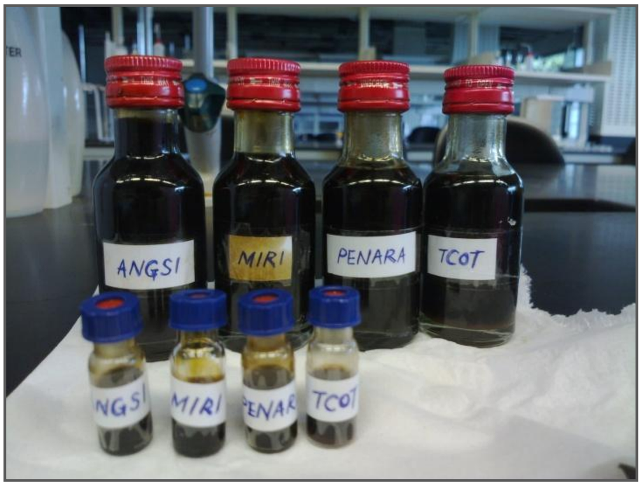


Figure 3.1-Crude Oil Samples from Different Field Location

As the samples come in large volume (around 4L to 5L), the samples are firstly heated to 80℃ for 8 hours in water bath to eliminate the thermal history as well as to avoid separation of heavy crudes and light crudes.

Figure 3.2-Preparation of Samples in Water Bath

Throughout the heating process, the samples are stirred from time to time to ensure complete dissolution and homogeneity. The samples are 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 hour is required for pre-heating before the commencement of future experimental measurements.

3.1.2 Gas Chromatography Mass Spectrometry (GCMS)

In this project, the GCMS used for 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 millimeters and phase thickness of 0.25 millimeters.

Figure 3.3-Shimadzu 5050 GC Coupled with Shimadzu 5973 with Mass Selective Detector

The procedures of the experiment are listed as below:

1. Oven temperature is set to be 120°C and hold for 3 minutes until it reaches maximum temperature of 270°C and hold for 40 minutes. Temperature increase rate is set to be 10°C/min.
2. At the temperature of 300°C, splitless injection is carried out.
3. Constant flow rate mode is set to be $2cm^3/min$.
4. Mass Spectrometry (MS) transfer line is set at 300°C.
5. Ion source is kept at 230°C.
6. Procedures 1 to 5 are repeated by using different crude oil samples.

3.1.3 Differential Scanning Calorimetry (DSC)

Prior to thermal analysis using DSC, Thermogravimetric Analysis or Thermal Gravimetric Analysis (TGA) is carried out to investigate the changes in weight in relation to temperature.

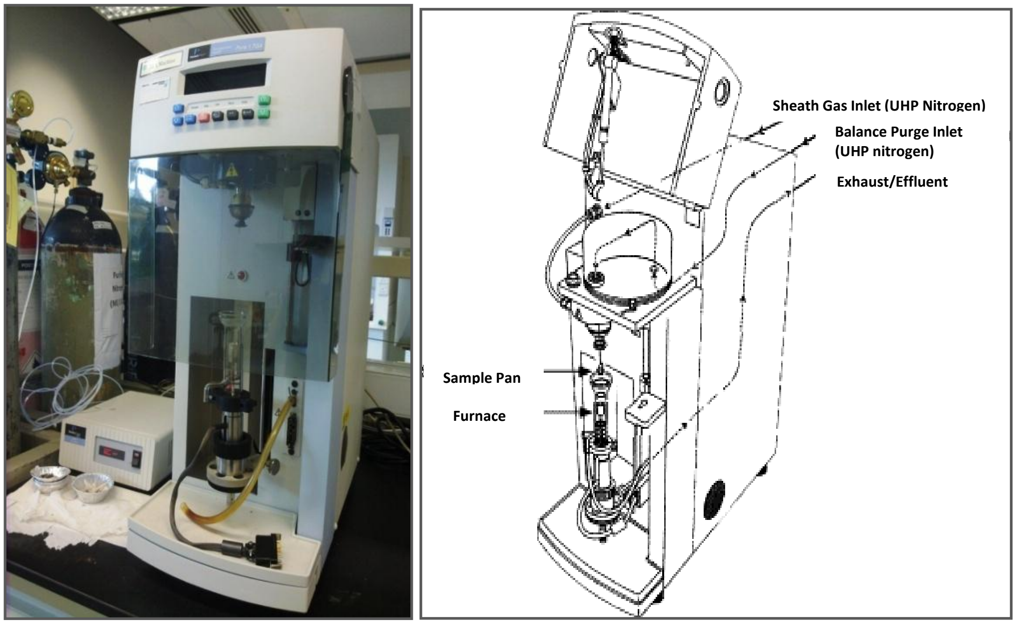


Figure 3.4-Experimental Machine for Thermal Gravimetric Analysis (TGA)

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 an act of heating a mixture to high enough temperature for the components to decompose into gas, where it dissociates into the air. Hence, the maximum heating temperature of DSC should be set lower than the TGA boiling point to prevent vaporization of crude oil samples.

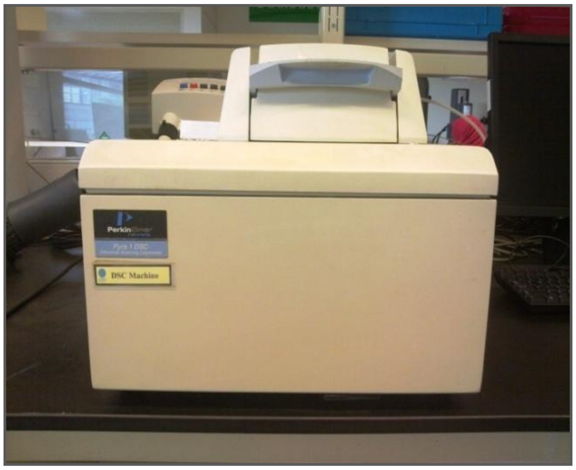


Figure 3.5-Differential Scanning Calorimetry (DSC)

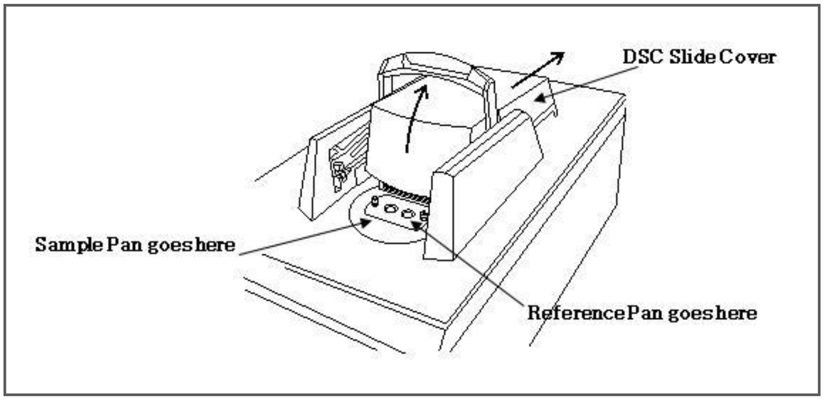


Figure 3.6-Differential Scanning Calorimetry Parts Labeling (DSC)

Samples are then sent for thermal analysis with maximum heating temperature below TGA decomposition temperature. 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.

The procedures of the experiment are listed as below:

For Thermogravimetry Analyzer (TGA):

1. 5mg of each samples are put in the machine for heating rate of 10°C/min.
2. The degrade/decomposition graph is observed.
3. From the obtained degrade/decomposition graph, determine the material's decomposition point (in the unit of °C) using software.

For Differential Scanning Calorimetry (DSC):

1. 5mg of each samples are prepared and put in the machine for analysis.
2. The experimental parameters are as below:
   - The samples are heated to 30°C and hold for 1 minute to achieve stable state.
   - The samples are heated from 30°C to 20°C below the material's decomposition point obtained from TGA.

- After the samples are heated to 20°C below the material's decomposition point obtained from TGA, hold the temperature for 1 minute to achieve stable state.
- The samples are cooled from 20°C below the melting point obtained from TGA to 30°C.
- The heating and cooling rate is 10°C/min.

3.1.4 Dewaxing Process

The wax fraction quantification in crude oils is performed by following the UOP46-85 (Universal Oil Products) method. Detailed procedures are listed as below:

1. Samples are dissolved in hexane and continually swirled on a hot plate.
2. Concentrated 18 molar sulphuric acid (H_2SO_4) is added to form an acidic tar with the asphaltene.
3. The oil-paraffin solution is decanted into a separator funnel and the asphaltene product is washed several times in warm hexane to recover as much wax as possible. Water is added to dilute the concentrated acid then the aqueous layer is removed upon separation.
4. A series of ammonium hydroxide and water washes are used to neutralize the sulphuric acid. Neutrality is checked by an aqueous phenolphthalein solution for colour change.
5. The hexane-wax solution is transferred to a flask and reduced by evaporation then redissolved in warm methylene chloride ($MeCl_2$). Dry ice is used to cool $MeCl_2$ to -30°C to ensure complete precipitation of wax in solution.
6. Solids are then removed by filtration under vacuum and the flask is rinsed with the chilled $MeCl_2$ several times.
7. Wax in the filter is dissolved in warm hexane and collected in tarred flask.
8. After evaporation of solvent, wax is weighted and the wax content is calculated.

3.2 Technique of Analysis

When all the necessary data and results are acquired from the experimental measurement, the graph of mol percent against carbon number distribution will be computed based on further analysis and studies. The Wax Appearance Temperature (WAT) and wax content will be determined through proposed methods by Jun Chen *et al* by finding Q (total thermal effect of wax precipitation) ratio of crude oil and its corresponding wax obtained as proposed in section 2.3.2 Thermal Analysis.

3.2.1 DSC Baseline Correction

Baseline correction needs to be performed for most DSC runs using Pyris software as the DSC thermogram cannot be completely level during the runs. In order to perform baseline correction, the following steps must be followed:

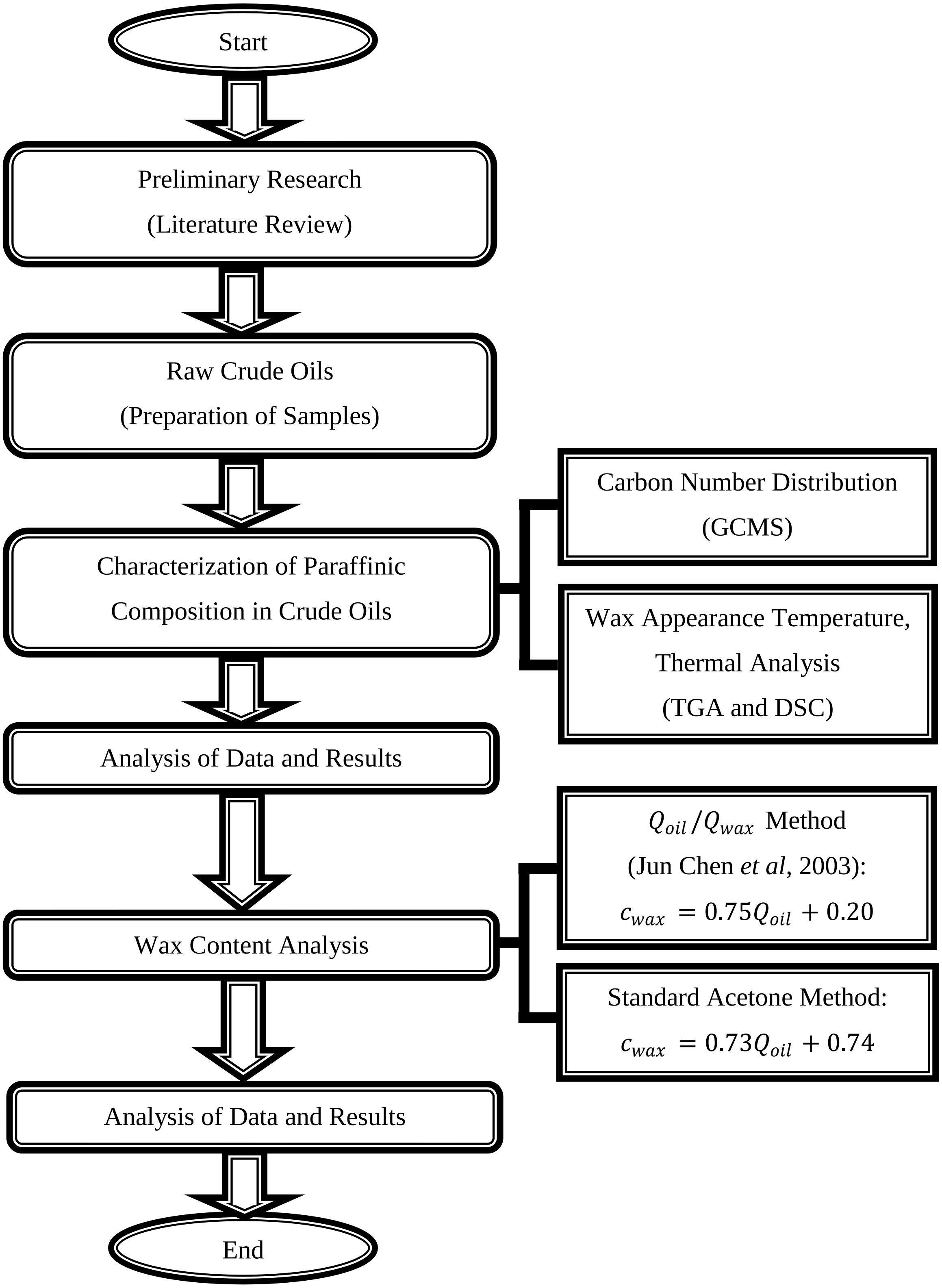
- The same run performed for crude oil sample should be performed with an empty sample pan with weight setting at zero for reference or comparison.
- The empty sample run is then subtracted from the original sample run to achieve baseline-corrected thermogram data.

3.2.2 DSC Base-line Computation

To perform base-line computation in DSC, the area, starting point, midpoint and end point of a peak transition should be determined. In heat flow curves, peak transitions are associated with melting, crystallization and curing.

After setting the left and right limits, sigmoidal baseline is used as the curve before the transition is at a different level than it is after the transition, which is very common in heat flow data. When sigmoidal baseline is chosen, tangents are drawn from the beginning of each specified limit. By selecting the function of “% Area Curve”, the percent area curve based on the peak area can be calculated and displayed.

3.3 Project Activities



3.4 Key Milestone

3.4.1 Timelines for Final Year Project 1

Detail/Week	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Selection of Project Topic	🟨	🟨												
Preliminary Research Work		🟨	🟨	🟨	🟨									
Submission of Extended Proposal Defense						🟥								
Proposal Defense								🟨	🟨					
Project Work Continues										🟨	🟨	🟨		
Submission of Interim Draft Report													🟥	
Submission of Interim Report														🟥

Colour Indication:

🟨	Duration of Task
🟥	Important Date for Task Submission

3.4.2 Timelines for Final Year Project 2

Detail/Week	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Project Work Continues	🟨	🟨	🟨	🟨	🟨	🟨	🟨								
Submission of Progress Report								🟥							
Project Work Continues								🟨	🟨	🟨	🟨	🟨	🟨		
Pre-EDX											🟥				
Submission of Draft Report												🟥			
Submission of Dissertation (Soft Bound)													🟥		
Submission of Technical Paper													🟥		
Oral Presentation														🟥	
Submission of Project Dissertation (Hard Bound)															🟥

Colour Indication:

🟨	Duration of Task
🟥	Important Date for Task Submission

3.5 Gantt Chart

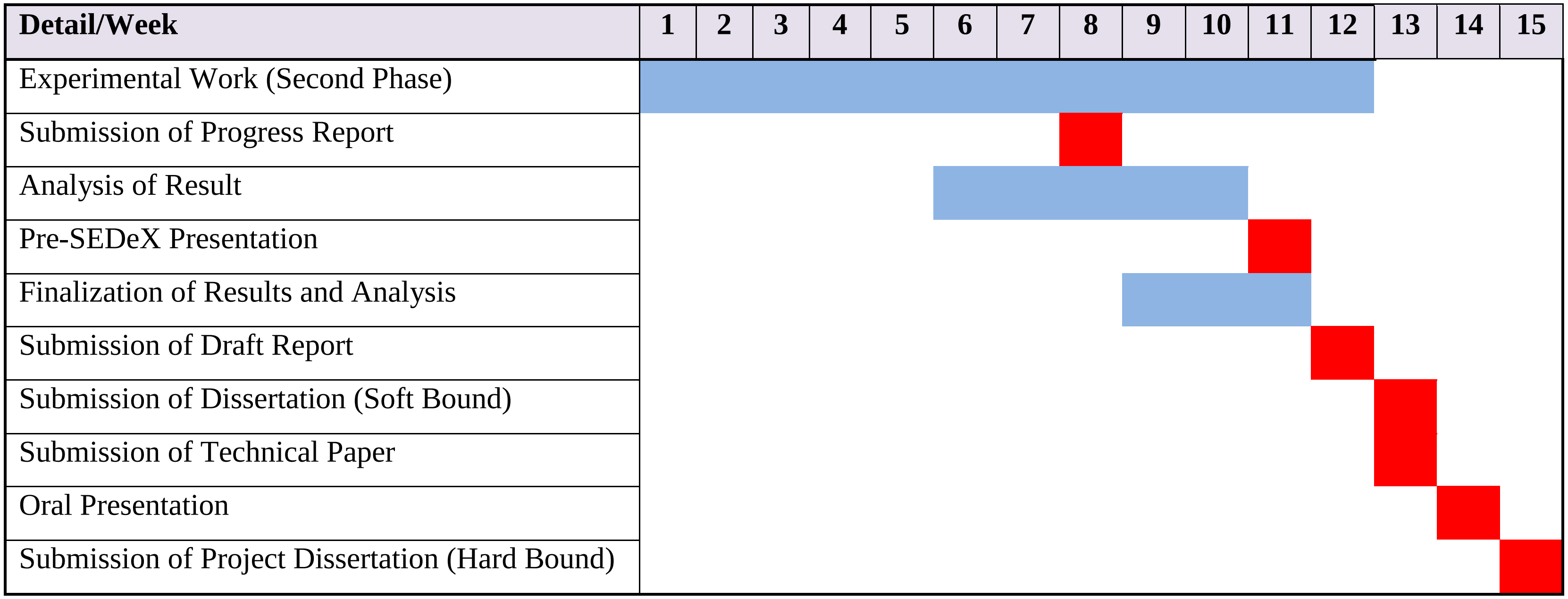
3.5.1 Suggested Gantt Chart for Final Year Project 1

Detail/Week	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Selection of Project Topic	🟦													
Preliminary Research Work/Literature Review		🟦	🟦	🟦										
Preparation of Samples				🟦	🟦									
Experimental Work (First Phase)						🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
Submission of Extended Proposal Defense						🟥								
Proposal Defense								🟦	🟦					
Analysis of Result									🟦	🟦	🟦	🟦	🟦	🟦
Submission of Interim Draft Report													🟥	
Submission of Interim Report														🟥

Colour Indication:

🟦 Duration of Task
🟥 Important Date for Task Submission

3.5.2 Suggested Gantt Chart for Final Year Project 2



Detail/Week	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Experimental Work (Second Phase)	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦			
Submission of Progress Report								🟥							
Analysis of Result						🟦	🟦	🟦	🟦	🟦					
Pre-SEDeX Presentation											🟥				
Finalization of Results and Analysis									🟦	🟦	🟦				
Submission of Draft Report												🟥			
Submission of Dissertation (Soft Bound)													🟥		
Submission of Technical Paper													🟥		
Oral Presentation														🟥	
Submission of Project Dissertation (Hard Bound)															🟥

Colour Indication:

🟦	Duration of Task
🟥	Important Date for Task Submission

CHAPTER 4

RESULT AND DISCUSSION

The results obtained from the various experiments using Gas Chromatography Mass Spectrometry (GCMS) and Differential Scanning Calorimetry (DSC) are presented and analysed in this chapter.

4.1 Gas Chromatography Mass Spectrometry

4.1.1 GCMS Chromatogram

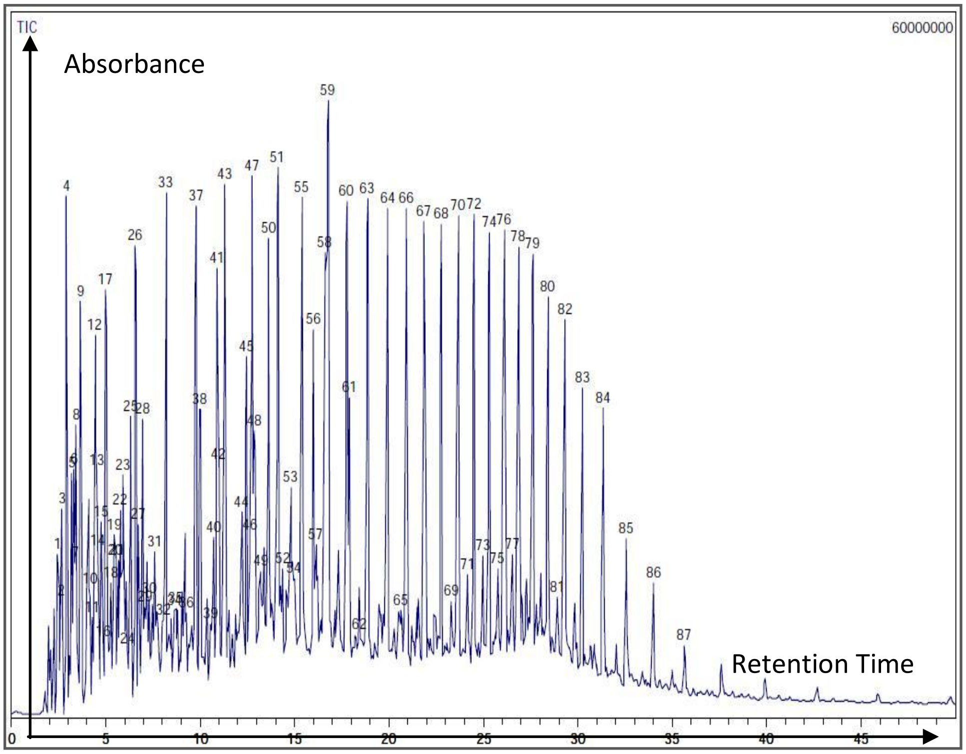


Figure 4.1-Chromatogram for Miri Waxy Crude Oil Sample

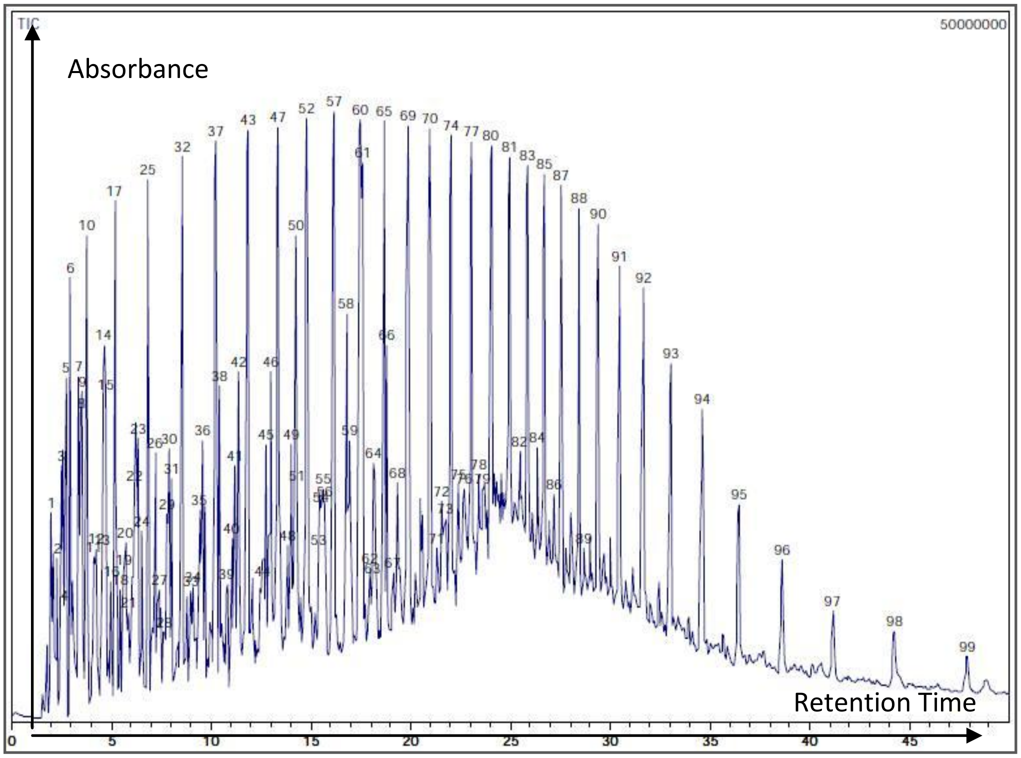


Figure 4.2-Chromatogram for Angsi Waxy Crude Oil Sample

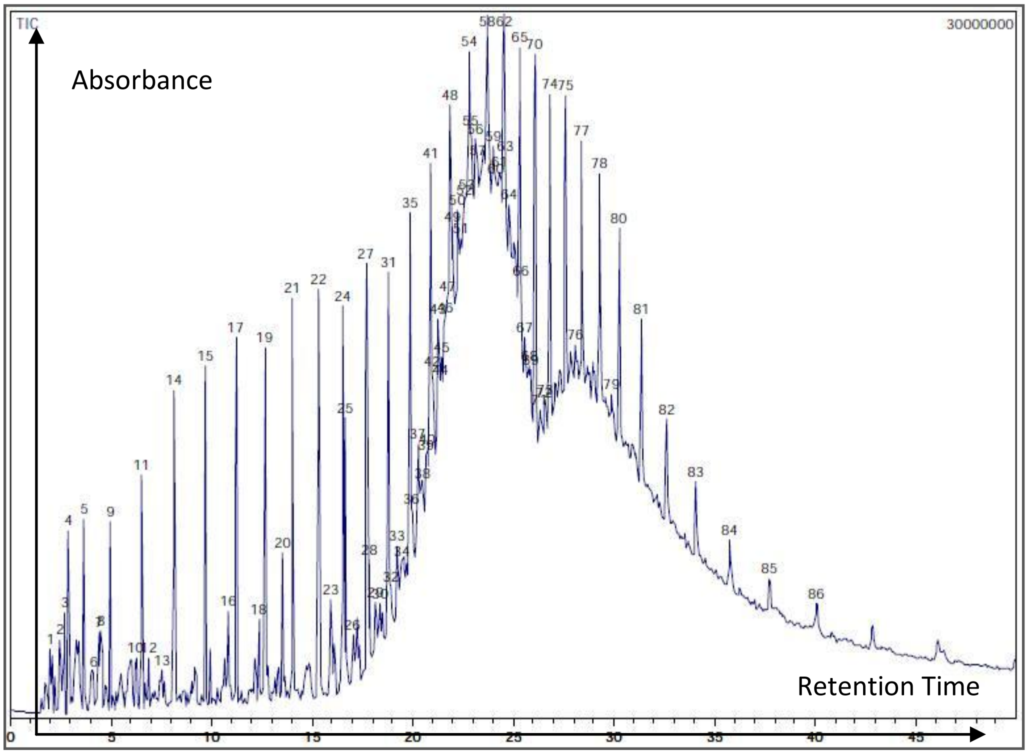


Figure 4.3-Chromatogram for PenaraWaxy Crude Oil Sample

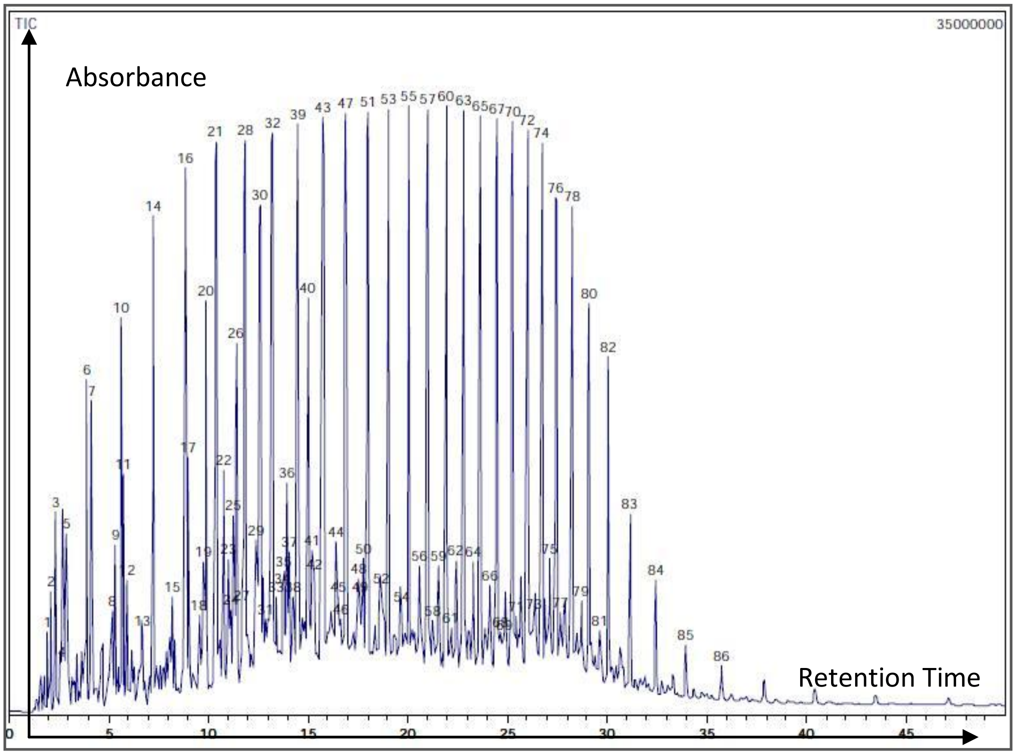
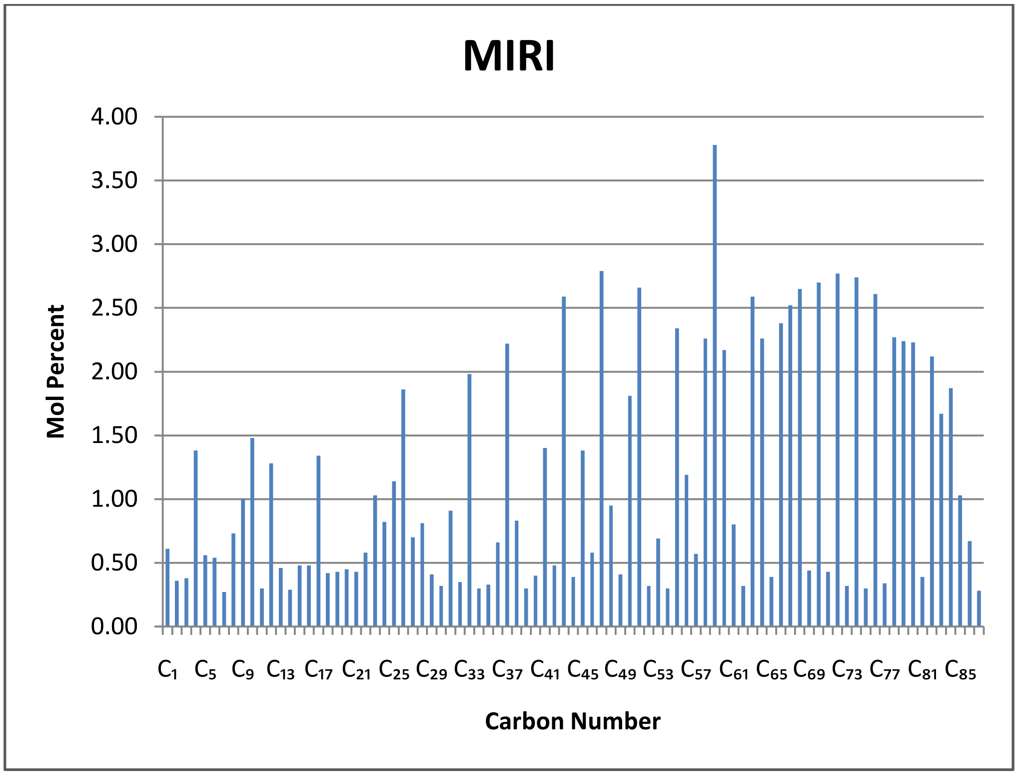


Figure 4.4-Chromatogram for Dulang Waxy Crude Oil Sample

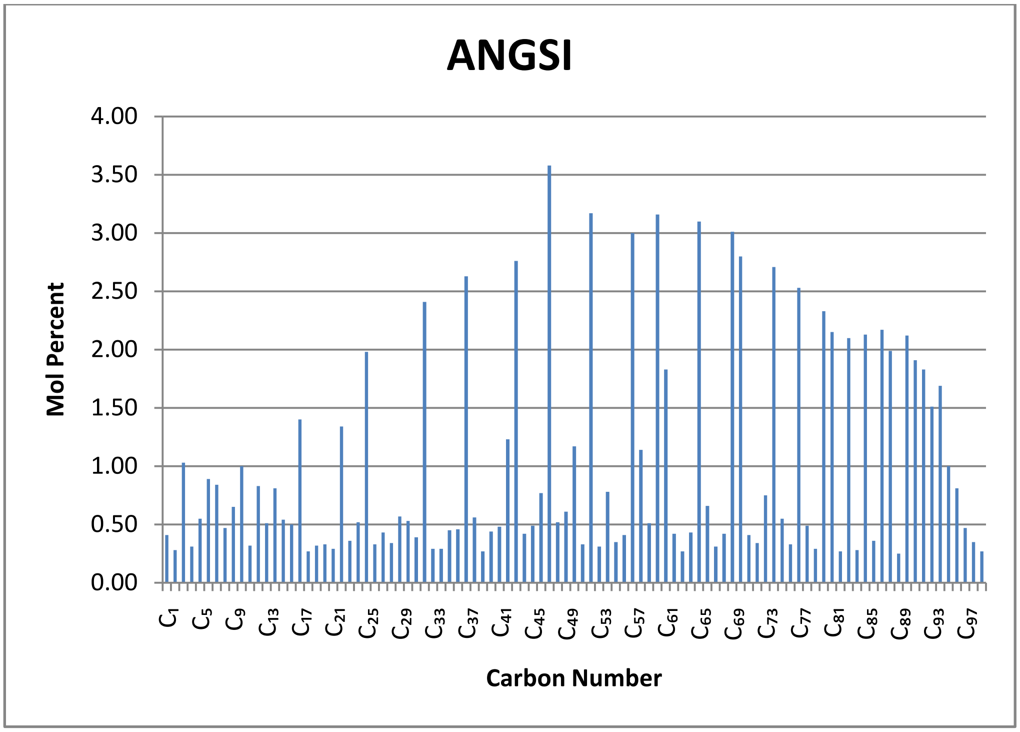
The objective for GCMS analysis is to obtain the hydrocarbon number distribution of the paraffinic composition in the waxy crudes samples. From the GCMS, the experimental measurement is shown in the form of chromatogram where the peaks represent the types of component present in the compound. The X-axis of the chromatogram represents the retention time (the lighter components are more towards the right of the chromatogram) while the Y-axis represents the absorbance. The retention time, types of components and concentrations can be obtained from the GCMS experimental measurements.

From the generated chromatograms, it is clear that the composition is predominantly of carbon number more than C_{20} and the components extend to the range of C_{86} and above. As per discussion in section 2.3.1, all the crude oil samples, especially the crude oil samples from Penara oil field,show significant presence of the paraffin wax which are the main contributing factor of wax deposition (spanning from $C_{20}$to C_{40}). Further analysis will be done to generate the histogram of mol percent versus carbon number for detailed and further analysis of the carbon number distribution in respective samples.

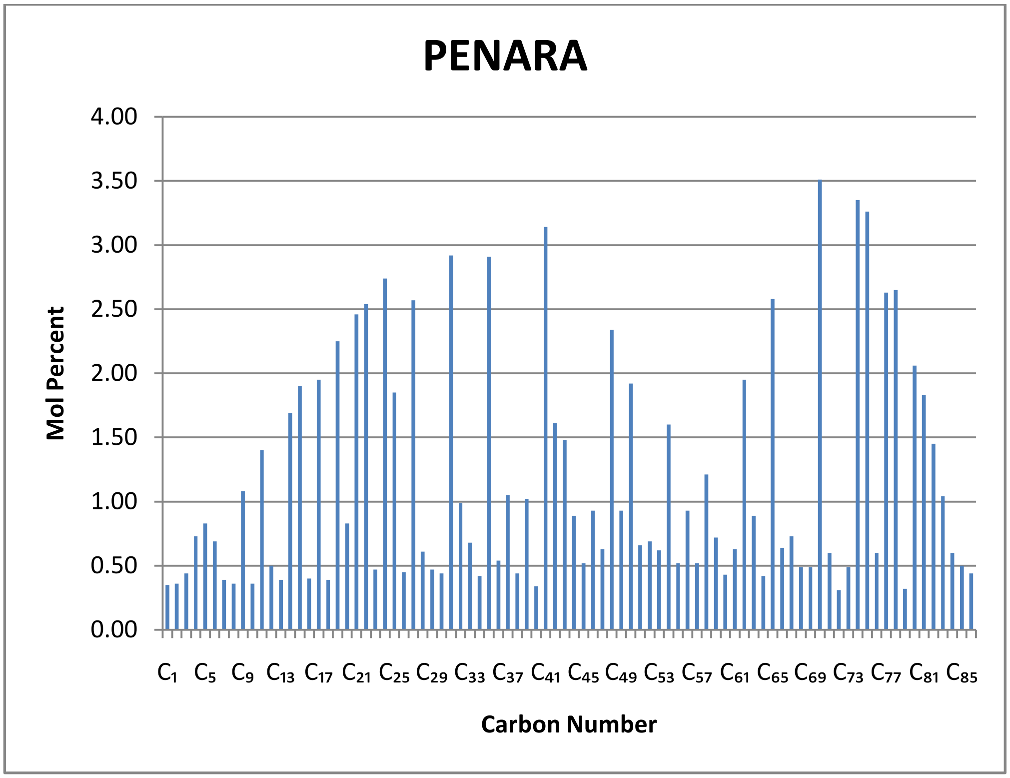
4.1.2 GCMS Data Analysis



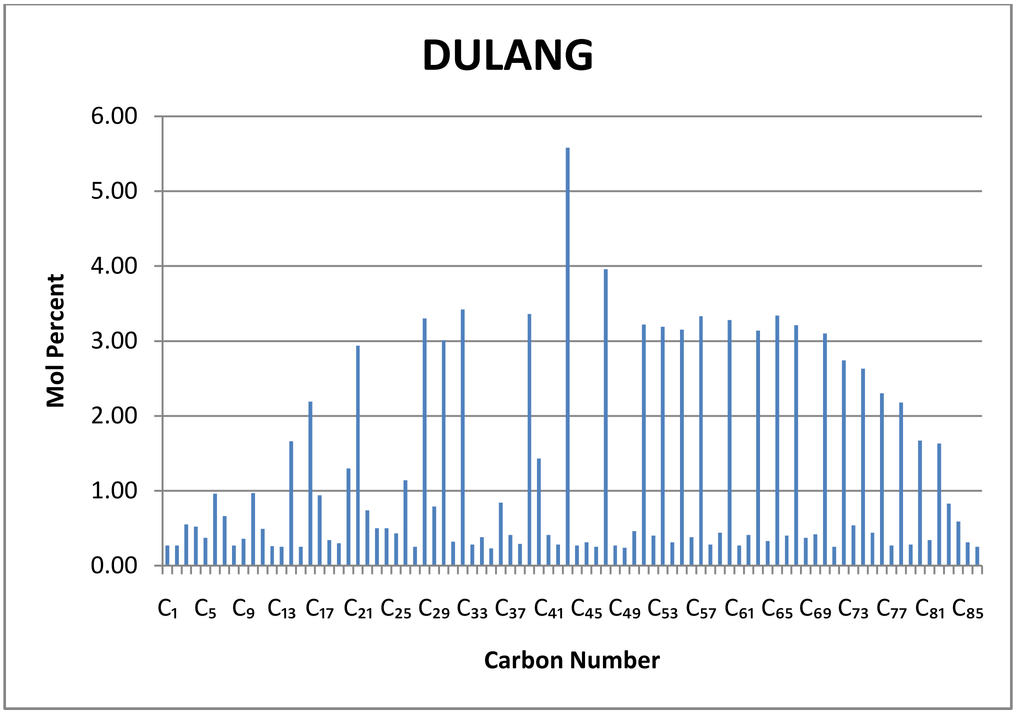
Graph4.1-Graph of Mol Percent Vs Carbon Number (Miri)



Graph 4.2-Graph of Mol Percent Vs Carbon Number (Angsi)



Graph 4.3-Graph of Mol Percent Vs Carbon Number (Penara)



Graph 4.4-Graph of Mol Percent Vs Carbon Number (Dulang)

** Refer to Appendix 1 to Appendix 4 for mol percent data of respective carbon number in table form.*

Table 4.1-Table of Cumulative Mol Percent (from $C_{20}$to C_{40}) for Each Sample

Samples	Miri	Angsi	Penara	Dulang
Cumulative Mol Percent (from C_{20} to C_{40})	16.83	15.21	26.74	25.86

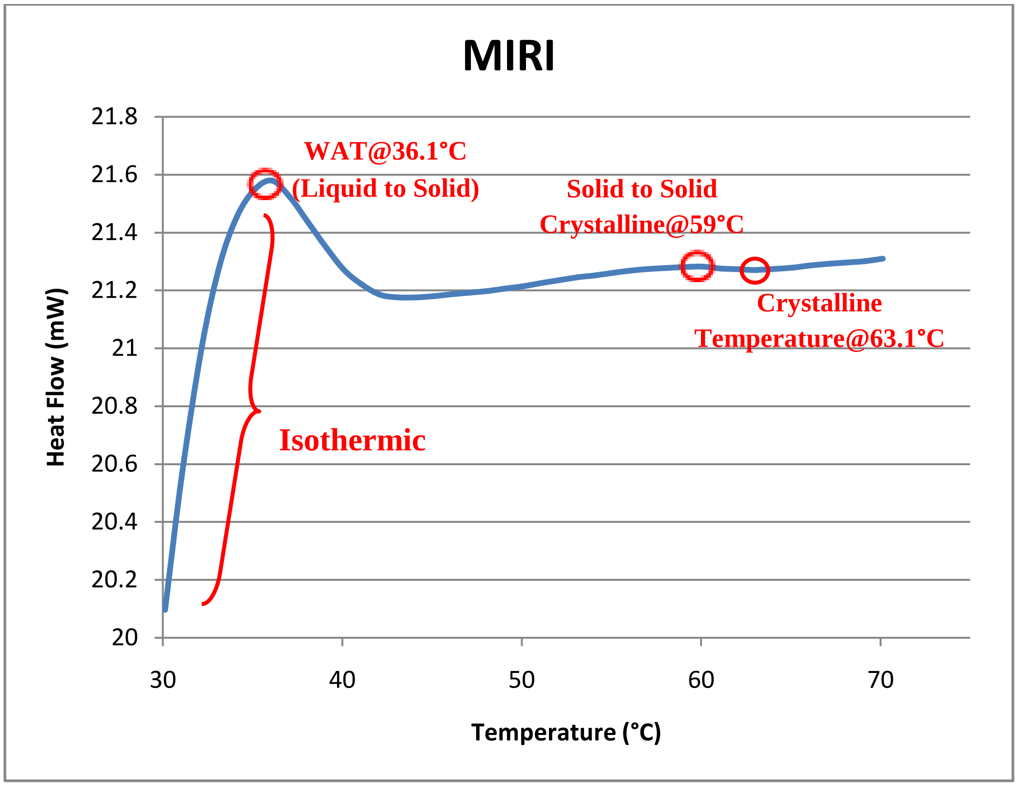
From the graph of mol percent vs carbon number distribution and table of cumulative mol percent (from C_{20} to C_{40}), crude oil samples from field location Penara and Dulang are observed to have higher percentage of paraffin wax compared to crude oil samples from field location Miri and Angsi. This will also directly affect the wax appearance temperature as paraffin waxes react and respond easily to temperature due to the straight chain structure.

From the GCMS data analysis, crude oil samples with high mol percent of paraffinic composition show possibility of having higher wax appearance temperature and wax content. To further proving the relation between paraffinic composition in crude oil samples, wax appearance temperature and wax content, DSC thermal analysis is utilized to investigate the temperature profile of each crude oil samples.

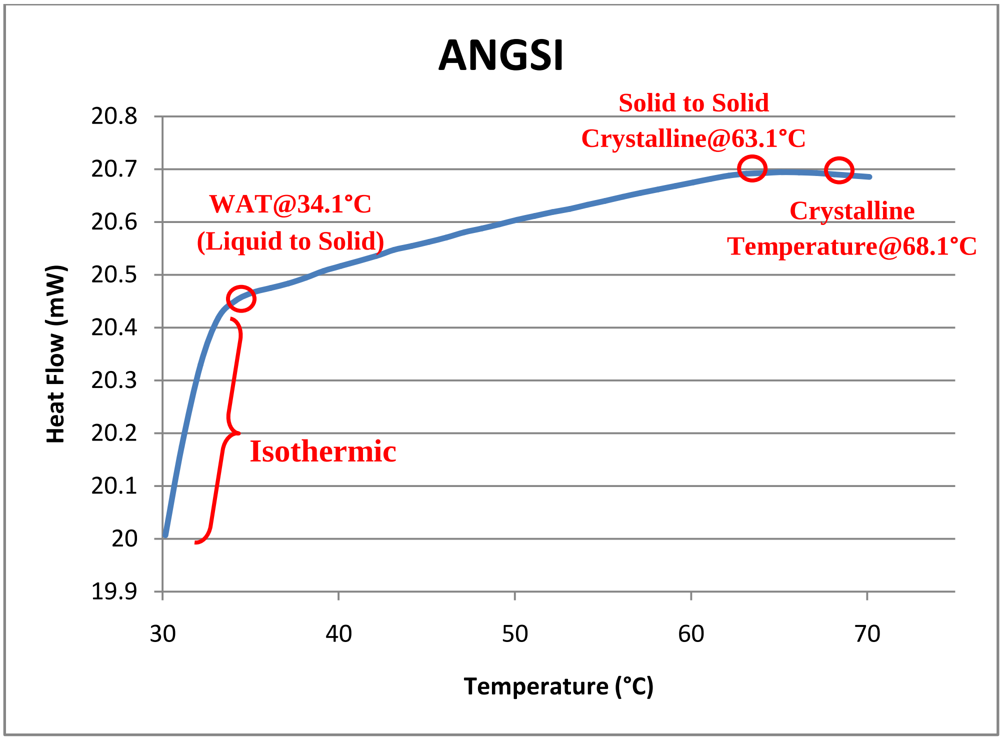
4.2 Differential Scanning Calorimetry (DSC)

From the DSC experimental measurement, wax appearance temperature (WAT) and wax content of the crude oil samples can be indentified. The results are shown as below.

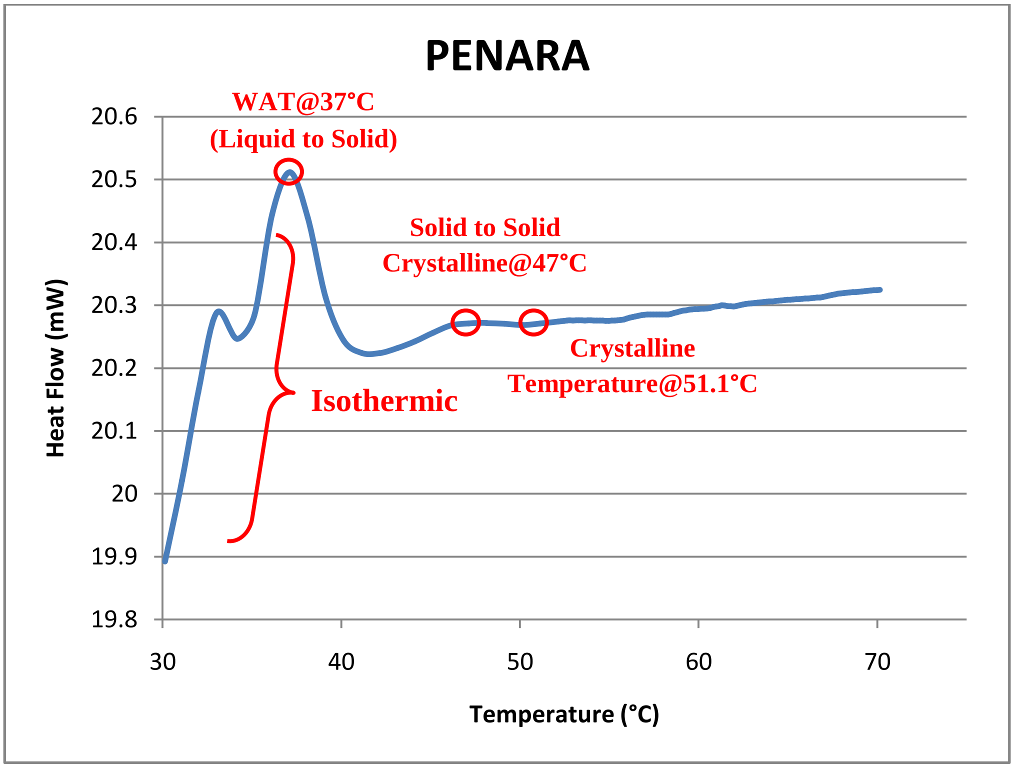
4.2.1 DSC Thermal Analysis



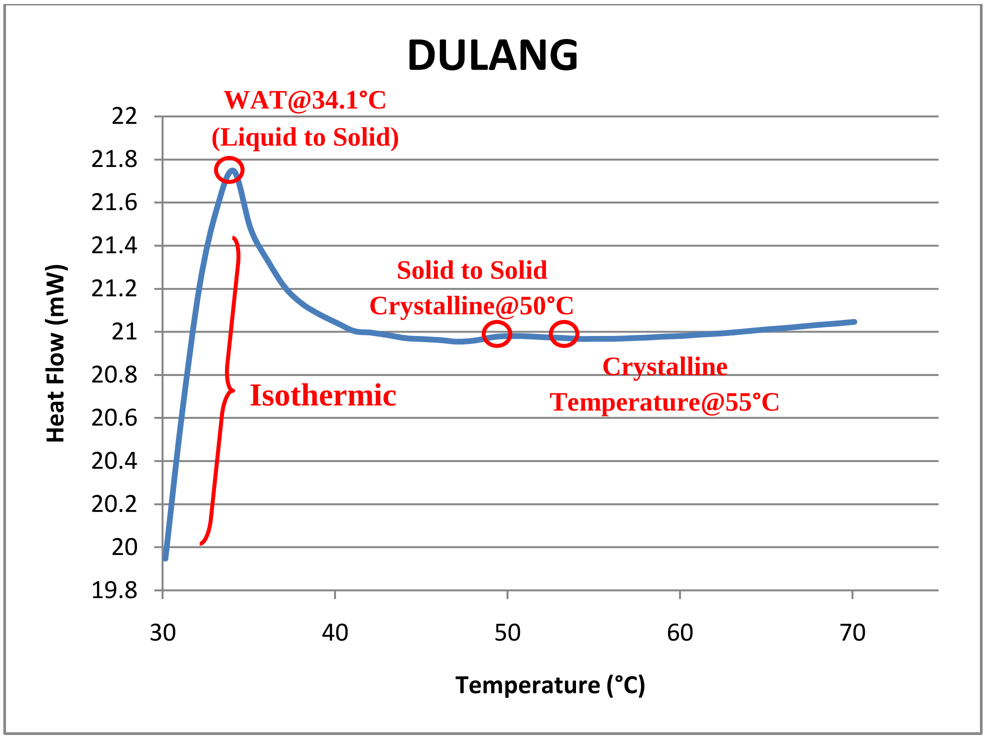
Graph4.5-Graph of Heat Flow Vs Temperature (Miri)



Graph 4.6-Graph of Heat Flow Vs Temperature (Angsi)



Graph 4.7-Graph of Heat Flow Vs Temperature (Penara)



Graph 4.8-Graph of Heat Flow Vs Temperature (Dulang)

Data of Wax Appearance Temperature, Solid to Solid Crystalline Temperature and Crystalline Temperature for each sample have been extracted from each graph and are shown in the table below:

Table 4.2-Table of Wax Appearance Temperature (WAT), Solid to Solid Crystalline Temperature and Crystalline Temperature for Each Sample.

Samples	Miri	Angsi	Penara	Dulang
Wax Appearance Temperature (°C)	36.1	34.1	37	34.1
Solid to Solid Crystalline (°C)	59	63.1	47	50
Crystalline Temperature (°C)	63.1	68.1	51.1	55

Compared to the experimental measurement obtained from GCMS, crude oil sample from Penara is proven to have the highest WAT. Due to the high mol percent of paraffin wax which react easily to temperature changes, crude oil sample from Penara also reveals the characteristic of having the lowest crystalline temperature, followed by crude oil sample from Dulang. Overall, crude oil sample from Penara takes the shortest period changing from WAT to crystalline temperature, showing the possibility of having high wax content.

4.2.2 DSC Wax Content Analysis

From the DSC measured result, the wax content also can be computed through empirical correlations as suggested by Jun Chen (2003), as per discussion in section 2.3.2. Base-line computation is established to determine the total thermal effect Q of the wax precipitation in the crude oil samples.

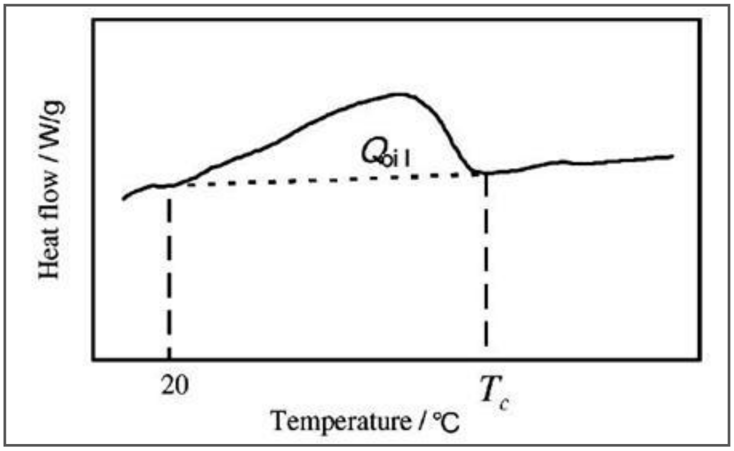


Figure 4.5-A sample of DSC Base-line Computation.

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 4.3-Table of Wax Content for Each Sample.

Samples	Miri	Angsi	Penara	Dulang
Wax Content (wt %)	28.90	25.83	33.65	27.35

From the base-line computation in DSC thermal analysis, the solid figure of wax content in each crude oil sample can be obtained. Crude oil sample from

Penara shows the highest wax content (wt%) compared to other crude oil samples.

Overall, crude oil sample with highest content of paraffinic composition is proven to have higher wax appearance temperature and wax content. Therefore, there is a linear relationship between the presences of paraffinic composition in crude oil and the wax deposition behaviour in pipeline systems.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

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. The carbon number distributions can be obtained by using Gas Chromatography Mass Spectrometry (GCMS); while, wax appearance temperature (WAT) and Wax-Temperature profile can be obtained from thermal analysis of Differential Scanning Calorimetry (DSC). Besides, the wax content of each sample can be calculated by utilizing the base-line computation in DSC thermal analysis.

The obtained results and analysis show that the paraffinic composition in crude oil will affect the behaviour of wax deposition in pipeline system. Crude oil with higher content of paraffinic compostion will result in higher wax appearance temperature as well as wax content.

Hence, the characterization of the paraffinic composition in crude oil samples from Miri, Angsi, Penara and Dulang can be investigated and established in order to assist the prediction of wax precipitation in respective field locations. The work can also be further expanded and developed to investigate more waxy crude samples from other 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 pipeline system.

5.2 Recommendations

For future study and further expansion of work, more waxy crude samples from different field locations in Malaysia can be obtained in order to establish the characterisation of paraffinic composition for respective field locations. The established characterization of paraffinic composition will be able to function as the foundation in establishing better solution in solving wax deposition issues.

In order to obtain higher data accuracy, more approaches can be utilized for data comparison. For example, to determine the wax appearance temperature (WAT), Cross Polar Microscopy (CPM) and viscometer can be used for data comparison with those generated from Differential Scanning Calorimetry (DSC).

Analysis of carbon number distribution can also be determined by simulated distillation (SIMDIS) using both gas chromatography mass spectrometry (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 [14]. There is also no risk of hydrocarbon decomposition at high temperature.

Collaboration with oil and gas production companies, such as PETRONAS Research Sdn. Bhd. is highly encouraged as the data accuracy can be improved by utilizing equipment with higher sensitivity.

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APPENDIX 1-Table of Mol Percent of Each Carbon Number (Miri)

Carbon Number	Mol %
C_{1}	0.61
C_{2}	0.36
C_{3}	0.38
C_{4}	1.38
C_{5}	0.56
C_{6}	0.54
C_{7}	0.27
C_{8}	0.73
C_{9}	1.00
C_{10}	1.48
C_{11}	0.30
C_{12}	1.28
C_{13}	0.46
C_{14}	0.29
C_{15}	0.48
C_{16}	0.48
C_{17}	1.34
C_{18}	0.42
C_{19}	0.43
C_{20}	0.45
C_{21}	0.43
C_{22}	0.58
C_{23}	1.03
C_{24}	0.82
C_{25}	1.14
C_{26}	1.86
C_{27}	0.70
C_{28}	0.81
C_{29}	0.41
C_{30}	0.32
C_{31}	0.91
C_{32}	0.35
C_{33}	1.98
C_{34}	0.30
C_{35}	0.33
C_{36}	0.66
C_{37}	2.22
C_{38}	0.83
C_{39}	0.30
C_{40}	0.40
C_{41}	1.40
C_{42}	0.48
C_{43}	2.59
C_{44}	0.39
C_{45}	1.38
C_{46}	0.58
C_{47}	2.79
C_{48}	0.95
C_{49}	0.41
C_{50}	1.81
C_{51}	2.66
C_{52}	0.32
C_{53}	0.69
C_{54}	0.30
C_{55}	2.34
C_{56}	1.19
C_{57}	0.57
C_{58}	2.26
C_{59}	3.78
C_{60}	2.17
C_{61}	0.80
C_{62}	0.32
C_{63}	2.59
C_{64}	2.26
C_{65}	0.39
C_{66}	2.38
C_{67}	2.52
C_{68}	2.65
C_{69}	0.44
C_{70}	2.70
C_{71}	0.43
C_{72}	2.77
C_{73}	0.32
C_{74}	2.74
C_{75}	0.30
C_{76}	2.61
C_{77}	0.34
C_{78}	2.27
C_{79}	2.24
C_{80}	2.23
C_{81}	0.39
C_{82}	2.12
C_{83}	1.67
C_{84}	1.87
C_{85}	1.03
C_{86}	0.67
C_{87}	0.28

APPENDIX 2-Table of Mol Percent of Each Carbon Number (Angsi)

Carbon Number	Mol %
C_{1}	0.41
C_{2}	0.28
C_{3}	1.03
C_{4}	0.31
C_{5}	0.55
C_{6}	0.89
C_{7}	0.84
C_{8}	0.47
C_{9}	0.65
C_{10}	1.00
C_{11}	0.32
C_{12}	0.83
C_{13}	0.51
C_{14}	0.81
C_{15}	0.54
C_{16}	0.50
C_{17}	1.40
C_{18}	0.27
C_{19}	0.32
C_{20}	0.33
C_{21}	0.29
C_{22}	1.34
C_{23}	0.36
C_{24}	0.52
C_{25}	1.98
C_{26}	0.33
C_{27}	0.43
C_{28}	0.34
C_{29}	0.57
C_{30}	0.53
C_{31}	0.39
C_{32}	2.41
C_{33}	0.29
C_{34}	0.29
C_{35}	0.45
C_{36}	0.46
C_{37}	2.63
C_{38}	0.56
C_{39}	0.27
C_{40}	0.44
C_{41}	0.48
C_{42}	1.23
C_{43}	2.76
C_{44}	0.42
C_{45}	0.49
C_{46}	0.77
C_{47}	3.58
C_{48}	0.52
C_{49}	0.61
C_{50}	1.17
C_{51}	0.33
C_{52}	3.17
C_{53}	0.31
C_{54}	0.78
C_{55}	0.35
C_{56}	0.41
C_{57}	3.00
C_{58}	1.14
C_{59}	0.51
C_{60}	3.16
C_{61}	1.83
C_{62}	0.42
C_{63}	0.27
C_{64}	0.43
C_{65}	3.10
C_{66}	0.66
C_{67}	0.31
C_{68}	0.42
C_{69}	3.01
C_{70}	2.80
C_{71}	0.41
C_{72}	0.34
C_{73}	0.75
C_{74}	2.71
C_{75}	0.55
C_{76}	0.33
C_{77}	2.53
C_{78}	0.49
C_{79}	0.29
C_{80}	2.33
C_{81}	2.15
C_{82}	0.27
C_{83}	2.10
C_{84}	0.28
C_{85}	2.13
C_{86}	0.36
C_{87}	2.17
C_{88}	1.99
C_{89}	0.25
C_{90}	2.12
C_{91}	1.91
C_{92}	1.83
C_{93}	1.51
C_{94}	1.69
C_{95}	1.00
C_{96}	0.81
C_{97}	0.47
C_{98}	0.35
C_{99}	0.27

APPENDIX 3-Table of Mol Percent of Each Carbon Number (Penara)

Carbon Number	Mol %
C_1	0.35
C_2	0.36
C_3	0.44
C_4	0.73
C_5	0.83
C_6	0.69
C_7	0.39
C_8	0.36
C_9	1.08
C_{10}	0.36
C_{11}	1.40
C_{12}	0.50
C_{13}	0.39
C_{14}	1.69
C_{15}	1.90
C_{16}	0.40
C_{17}	1.95
C_{18}	0.39
C_{19}	2.25
C_{20}	0.83
C_{21}	2.46
C_{22}	2.54
C_{23}	0.47
C_{24}	2.74
C_{25}	1.85
C_{26}	0.45
C_{27}	2.57
C_{28}	0.61
C_{29}	0.47
C_{30}	0.44
C_{31}	2.92
C_{32}	0.99
C_{33}	0.68
C_{34}	0.42
C_{35}	2.91
C_{36}	0.54
C_{37}	1.05
C_{38}	0.44
C_{39}	1.02
C_{40}	0.34
C_{41}	3.14
C_{42}	1.61
C_{43}	1.48
C_{44}	0.89
C_{45}	0.52
C_{46}	0.93
C_{47}	0.63
C_{48}	2.34
C_{49}	0.93
C_{50}	1.92
C_{51}	0.66
C_{52}	0.69
C_{53}	0.62
C_{54}	1.60
C_{55}	0.52
C_{56}	0.93
C_{57}	0.52
C_{58}	1.21
C_{59}	0.72
C_{60}	0.43
C_{61}	0.63
C_{62}	1.95
C_{63}	0.89
C_{64}	0.42
C_{65}	2.58
C_{66}	0.64
C_{67}	0.73
C_{68}	0.49
C_{69}	0.49
C_{70}	3.51
C_{71}	0.60
C_{72}	0.31
C_{73}	0.49
C_{74}	3.35
C_{75}	3.26
C_{76}	0.60
C_{77}	2.63
C_{78}	2.65
C_{79}	0.32
C_{80}	2.06
C_{81}	1.83
C_{82}	1.45
C_{83}	1.04
C_{84}	0.60
C_{85}	0.50
C_{86}	0.44

APPENDIX 4-Table of Mol Percent of Each Carbon Number (Dulang)

Carbon Number	Mol %
C_{1}	0.27
C_{2}	0.27
C_{3}	0.55
C_{4}	0.52
C_{5}	0.37
C_{6}	0.96
C_{7}	0.66
C_{8}	0.27
C_{9}	0.36
C_{10}	0.97
C_{11}	0.49
C_{12}	0.26
C_{13}	0.25
C_{14}	1.66
C_{15}	0.25
C_{16}	2.19
C_{17}	0.94
C_{18}	0.34
C_{19}	0.30
C_{20}	1.30
C_{21}	2.94
C_{22}	0.74
C_{23}	0.50
C_{24}	0.50
C_{25}	0.43
C_{26}	1.14
C_{27}	0.25
C_{28}	3.30
C_{29}	0.79
C_{30}	3.01
C_{31}	0.32
C_{32}	3.42
C_{33}	0.28
C_{34}	0.38
C_{35}	0.23
C_{36}	0.84
C_{37}	0.41
C_{38}	0.29
C_{39}	3.36
C_{40}	1.43
C_{41}	0.41
C_{42}	0.28
C_{43}	5.58
C_{44}	0.27
C_{45}	0.31
C_{46}	0.25
C_{47}	3.96
C_{48}	0.27
C_{49}	0.24
C_{50}	0.46
C_{51}	3.22
C_{52}	0.40
C_{53}	3.19
C_{54}	0.31
C_{55}	3.15
C_{56}	0.38
C_{57}	3.33
C_{58}	0.28
C_{59}	0.44
C_{60}	3.28
C_{61}	0.27
C_{62}	0.41
C_{63}	3.14
C_{64}	0.33
C_{65}	3.34
C_{66}	0.40
C_{67}	3.21
C_{68}	0.37
C_{69}	0.42
C_{70}	3.10
C_{71}	0.25
C_{72}	2.74
C_{73}	0.54
C_{74}	2.63
C_{75}	0.44
C_{76}	2.30
C_{77}	0.27
C_{78}	2.18
C_{79}	0.28
C_{80}	1.67
C_{81}	0.34
C_{82}	1.63
C_{83}	0.83
C_{84}	0.59
C_{85}	0.31
C_{86}	0.25