CHARACTERIZATION OF WAXY AND ASPHALTENIC CRUDE OIL USING SARA ANALYSIS

By

Mohamad Hazwan Bin Yusoff @ Mohd Yusoff

Dissertation submitted in partial fulfilment of

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Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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(12656)

A project dissertation submitted to the

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Approved by,

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(Dr Aliyu Adebayor Sulaimon)

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR

31750 TRONOH, PERAK

May 2013

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.

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(MOHAMAD HAZWAN BIN YUSOFF @ MOHD YUSOFF)

ABSTRACT

Flow assurance is the term used to describe the issues that distort the flow of oil, water and gas in production and transportation system. The problems are mainly due to waxes and asphaltenes deposition as temperature and pressure inside wellbore and pipeline changes. Wax will start to precipitate when temperature falls below cloud point or known as wax appearance temperature (WAT) as it travels from reservoir to surface. Experimental data are very limited to confirm the existing prediction models for different type of crude oils.

The focus of this research were to study the characteristic of crude oil in term of SARA (saturates, aromatics, resins and asphaltenes) fractions and carbon distribution by using high performance liquid chromatography (HPLC) and gas chromatography mass spectrometry (GC-MS) respectively. Differential scanning calorimetry (DSC) and density meter were used to measure the WAT of crude oils. Comparisons of WAT obtained from DSC and density meter were provided and the result shows a good agreement between DSC and density meter technique. Colloidal instability index (CII) was used to correlate the composition of the crude oil with the potential of solid precipitation. A study on the effect of continuous carbon dioxide (CO_2) injection on wax appearance temperature of crude oil was provided.

For this research, five crude oil samples from different location (Dulang, Tapis, Miri, Dubai and Arab) were analysed. Each sample has different characteristic hence resulted in different depositional problem. The CII value for Dulang, Arab, Tapis, Miri, and Dubai is 4.09, 1.21, 5.05, 0.64 and 0.90 accordingly. The SARA fractions, WAT, and carbon number distribution of the samples were obtained. The results shows that crude oil samples with higher paraffinic composition have higher wax appearance temperature and wax content than crude oil samples with lower paraffinic composition.

As a conclusion, Dulang, Tapis, Arab and Dubai crude oils have high tendency for asphaltenes deposition while Miri crude oil has low tendency for asphaltenes deposition. The study shows that the CO_2 injection will decrease the WAT as tested on Dulang crude oil.

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ABBREVIATIONS AND NOMENCLATURE

AOP	=	Asphaltene Onset Pressure
API	=	American Petroleum Institute
ART	=	Acoustic Resonance Technique
CF	=	Cold Finger
CII	=	Colloidal Instability Index
CPM	=	Cross Polar Microscopy
DSC	=	Differential Scanning Calorimetry
EOR	=	Enhance Oil Recovery
FD	=	Filter Plugging
FT-IR	=	Fourier Transform Infrared Spectroscopy
GCMS	=	Gas Chromatography Mass Spectrometry
HPLC	=	High Pressure Liquid Chromatography
LST	=	Light Scattering Technique
LT	=	Light Transmittance
NMR	=	Nuclear Magnetic Resonance
PVT	=	Pressure, Volume, Temperature
RI	=	Refractive Index
SARA	=	Saturates, Aromatics, Resins, Asphaltenes
SDS	=	Solid Detection System
STO	=	Stock Tank Oil
TLC-FID	=	Thin Layer Chromatography Flame Ionization Detection
UOP	=	Universal Oil Product
UV	=	Ultraviolet
VOC	=	Volatile Organic Compound
WAT	=	Wax Appearance Temperature
WDT	=	Wax Disappearance Temperature

CHAPTER ONE

INTRODUCTION

1.1 Background of Study

Since the first oil well that had been drilled in 1859, billion barrels of crude oil had been produced from different region and field. The characterization of each crude oil is distinctive from each other. It can be light crude oil or heavy crude oil depending on its density and other properties. Besides, heavy crude oil may contain a large amount of wax, asphaltene and other substance that can cause serious problem during production operation.

Wax deposition occurs as crude oil generally has n-paraffin 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. In subsea completion (where flow lines on the ocean floor ranges about 1.5^{o}C to 5^{o}C), each wax component becomes less soluble until the higher molecular weight components solidify. The onset of crystallization is known as the wax appearance temperature (WAT) and as the temperature drop 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 (Li & Zhang, 2003).

In this study, Saturate, Aromatic, Resin and Asphaltene (SARA) analysis is used to identify the characterization of the crude oil. This area of study was first introduced by Jewell *et al*. (1972) where they developed the basis for SARA fractionation. It is the method that categorizes crude oil components based on their polarity and polarizability. The saturate is a nonpolar material such as paraffin while aromatics are slightly more polarizable. Both resins and asphaltenes have polar substituents.

Issues on asphaltene and solid precipitation have always been highlighted as one of the major fouling precursors. A small change in aromatics, resin and saturates or temperature can initiate asphaltene dropouts.

1.2 Problem Statement

As the demand increases and the global supply of light crude oil are exhausted, production and refinery are extremely moving towards heavy conventional and unconventional crude oil. Therefore, engineers are struggled to overcome the challenge of handling waxy and asphaltenic crude oil which is proved to cause major problem in production, transportation and processing process. Flow assurance is the term used to describe the issues that distort the flow of oil, gas and water in the production or transportation systems.

Thus, this study is conducted to analyse and compare the characteristic of the waxy and asphaltenic crude oil so that we will have more knowledge on its behaviour for the betterment of the oil and gas industry. The research is very significant as the result gave the composition of the crude oil. The data is very important for the design of production and stimulation program.

1.3 Objective

The objective of the study is mainly to know the details of each component of samples of crude oil such as saturates, aromatics, resins and any others substance that may appear in the crude oil. Different reservoir or field will produce different crude oil with different composition. Therefore, this research will aims to:

1) Record and analyse the composition of crude oil samples by using SARA analysis.
2) Determine the wax appearance temperature (WAT).

1.4 Scope of Studies

The project is based on experimental measurement and analysis. The first part is to determine the characteristic of paraffinic composition in the crude oil. The experiment focuses on the following properties: carbon number distribution (C_{20} – C_{40}), WAT as well as wax content. The study of carbon number distribution, WAT and wax content is conducted using Gas Chromatography Mass Spectrometry

(GCMS), Differential Scanning Calorimetry (DSC) and UOP-46 method respectively. Results from GCMS are used to analyse the paraffin wax ranging from C_{20} to C_{40}. For many type of crude oil, analyses of the wax reveal a good correlation with various parameters such as viscosity and WAT.

1.5 Relevancy and Feasibility of Study

This project is relevant to the author as a Petroleum Engineering student who had already completed many courses related to production and deliverability of the fluid. Problems related with wax deposition are very costly because of cleaning operation as well as production downtime. Therefore, accurate prediction of WAT and wax content formed at certain environment are very crucial for optimum production operation. This project aims to provide characteristic of crude oil in order to assist future development and production plan especially for Malaysian's oil field.

The development and completion of the project is feasible judging from the objectives and scope of studies included in the research. The overall period to complete the research is approximately 8 months. Moreover, this research is considered as feasible as all the equipment including materials and apparatus are available in laboratory of Universiti Teknologi PETRONAS. Time constraint also has been considered and this project has completed within the time specified in the project Gantt chart.

CHAPTER TWO

LITERATURE REVIEW

This section presents a review of the literature on crude oil characterization, characteristics of wax and asphaltene, problems and issues related to wax and asphaltene precipitation as well as SARA analysis method that are being used in industry. Besides, a review on the factors that affect the behaviour of waxy and asphaltenic crude oil is also presented.

2.1 Crude oil characterization

Crude oil is a mixture of naturally occurring hydrocarbons, organic compound of nitrogen, sulphur and oxygen, and small amount of metallic constituents like iron. The origin of crude oil can have a significant effect on its composition hence have wide variety in volatility, density, colour and viscosity. Crude oil can be classified as light oil, heavy oil or bitumen and uses ^{o}API as a measure of viscosity as shown in Table 1.

Crude oil can be characterized into pseudo-components based on density, chemical composition, boiling cut, carbon distribution, H/C atomic ratio and solubility class (Pedersen & Christensen, 2007). The techniques depend on the oil type and the required information of its property for pseudo-component. The process of obtaining the composition of crude oil is complex, time consuming and very expensive. They need a lot of solvents and each procedure can last for days. However, the procedure can be simplified by assuming that the petroleum consists of a number of light discrete components and a heavy end. The heavy end is considered to be part of four major fractions of similar species (Mansoori *et al*., 2006).

Table 1: Classification of crude oil (Tharanivasan, 2012)

Crude Oil Type	Viscosity (mPa's)	Density (kg/m^3)	^{o}API
Light oil	<100	<934	>20
Heavy oil	100-100,000	934-1000	10-20
Bitumen	>100,000	>1000	<10

2.2 Characteristics of wax and asphaltene

Heavy oil is known to have heavy compounds like waxes and asphaltenes. Wax is a group of normal paraffin that contain 16 or more carbon atoms that will change to crystalline solid substances at 20^{o}C. The wax in crude oil is a mixture of normal hydrocarbons with different carbon number distributions which can be identified by using Gas Chromatography (GC) as in figure 1. Macrocrystalline wax (C_{18} - C_{36}) and microcrystalline wax (C_{30} - C_{60}) are two different type of wax that can be found in crude oil. Both of them are made up of aligned paraffinic and naphthenic molecules (Kok & Saracoglu, 2000).

Macrocrystalline waxes are mainly composed of straight-chain paraffins (n-alkanes) with different chain length while microcrystalline waxes contains high amount of isoparaffins and naphthenes (Elsharkawy *et al.*, 1999). The straight-chain structure of macrocrystalline waxes causes it to be more sensitive to temperature changes. The existence of solid particles will cause the flow behavior to change from Newtonian to non-Newtonian.

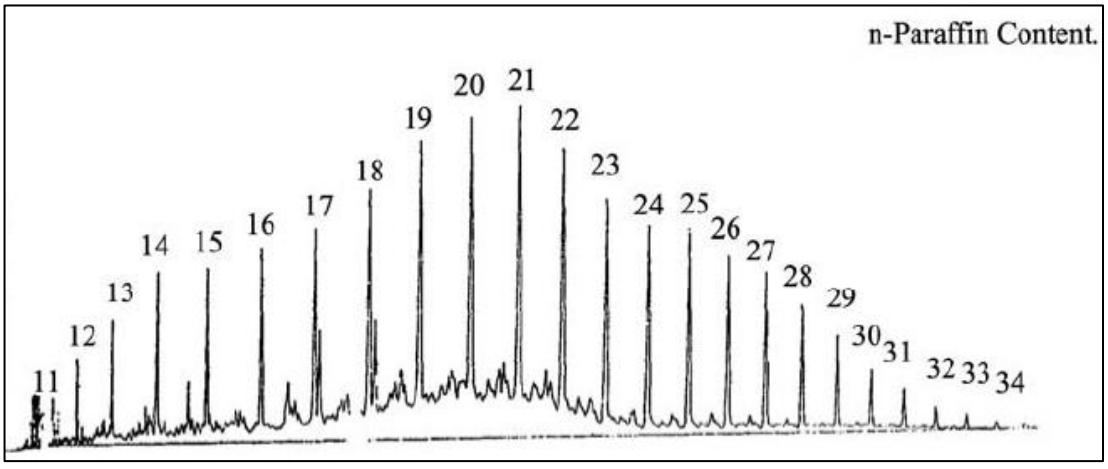

Figure 1: Carbon number distribution of n-paraffin fraction separated from gas oil (Khidr *et al.*, 2007)

Asphaltenes are defined as a solubility class of petroleum, which precipitate from crude oil by the addition of an excess amount of n-alkane solvent like *n*-pentane and are soluble in aromatic solvents like benzene. "Pentane (C_5)-asphaltenes" and "heptane (C_7)-asphaltenes" is the name of the precipitate produced when adding the *n*-pentane and *n*-heptane to the oil respectively. The oil is called "asphaltenes-free" if there is no precipitate. Speight (1999) tabulated the elemental composition of asphaltenes from different crude oil of different region which are Canada, Iran, Kuwait and Venezuela as in Table 2.

Table 2: Elemental composition of asphaltenes from world sources (Speight, 1999)

	Canada	Iran	Kuwait	Venezuela
Carbon (wt %)	79.0-88.7	83.7	81.6-82.4	81.1-84.7
Hydrogen (wt %)	6.9-11.1	7.8	7.8-8.1	7.8-8.3
Nitrogen (wt %)	0.7-2.8	1.7	0.6-1.7	0.2-2.0
Sulphur (wt %)	0.3-8.1	5.8	7.4-8.0	2.7-6.9
Oxygen (wt %)	0.4-3.9	1.0	0.6-1.8	1.0-4.2
H/C Ratio	0.98-1.56	1.19	1.14-1.19	1.13-1.19
N/C Ratio	0.007-0.029	0.017	0.008-0.017	0.002-0.02
S/C Ratio	0.001-0.038	0.026	0.034-0.039	0.012-0.032
O/C Ratio	0.004-0.037	0.009	0.005-0.017	0.013-0.039

2.3 Problems and issues related to wax and asphaltene precipitation

Asphaltene is the heaviest component compared to saturates, aromatic, and resin in crude oil and it is readily dissolved in crude oil. When it is separated from the crude oil because of composition change or pressure loss, asphaltene may deposit on the rock surface and plug some pore throats that will cause more flow resistance for oil in porous medium. After some period of time, the deposits at certain concentration can cause major formation damage (Choiri, 2010).

Asphaltenes from crude oils can also be deposited inside of refinery's pipeline as shown in figure 2. It will reduce the flow of crude oil and the process is described to be like coronary artery disease and cause significant problems further downstream.

Figure 2: Asphaltenes deposit formed on the inside of a pipeline in a refinery (McKenna, 2009)

The main factors that contribute to the precipitation of asphaltenes are temperature, pressure and composition variation due to gas injection and phase separation (Goual, 2012). Apart from that, the process of refining heavy oil is very challenging as asphaltene can cause fouling and coking while wettability alteration and formation damage can happen if the asphaltenes is absorbed by the mineral rocks.

Solids depositions which are asphaltenes and wax in reservoir, subsurface and surface equipment, wellhead equipment, tanks and separator can lead to problems in operation which will reduce the production rate significantly (Mansoori & Leontartis, 1988). Krishna (1989) stated that gelling process may happen at 2% of precipitated wax. Clean up and downtime due to plugging in pipelines is very costly especially in offshore oil production as shown in in Table 3.

Table 3: Additional cost due to occurrence of asphaltene deposit problems (Fargas *et al.*, 2010)

Operation	**Cost**
Removal of deposit	$300k-$3,500K/well
Side track	$50,000K/well
Downtime	$700k/day (for production of 7,000BPD)

2.4 SARA analysis

The SARA analysis defines the content of saturate aromatics, resins and asphaltenes in crude oil, heavy cuts and residues. The data is beneficial in refinery design and operations. The analysis is preparative which means that the test provides enough samples of saturate, aromatics, resins and asphaltenes for further testing and analysis (Speight, 1991). The compound is separated in different stages. The first stage is to precipitate the asphaltenes by *n*-heptane. Deasphalted oil or known as Maltenes is subjected to liquid chromatography which has similar principles as gas chromatography. In this case, the compound is eluted from a packed column by a liquid. The saturated hydrocarbon are eluted by *n*–heptane, the aromatics by a 2:1 volume mixture of *n*-heptane and toluene and the resins by an equal volume mixture of methanol, toluene and dichloromethane by using ASTM D4124 (Fahim *et al*., 2010).

Measurements the result from SARA analysis of different method will be always different therefore it is not comparable (Fan, 2002). The TLC-FID technique is not suitable for oil with medium gravity if there is no additional analysis to include components that boil at temperature up to 250^{o}C. It is recommended to use high pressure liquid chromatography (HPLC) method as it will yield similar result as time-consuming ASTM method.

According to Tharanivasan (2012), there are two procedures for SARA fractionation which are University of Calgary procedure and DBR procedure which based on traditional ASTM method as shown in figure 3 and figure 4 respectively.

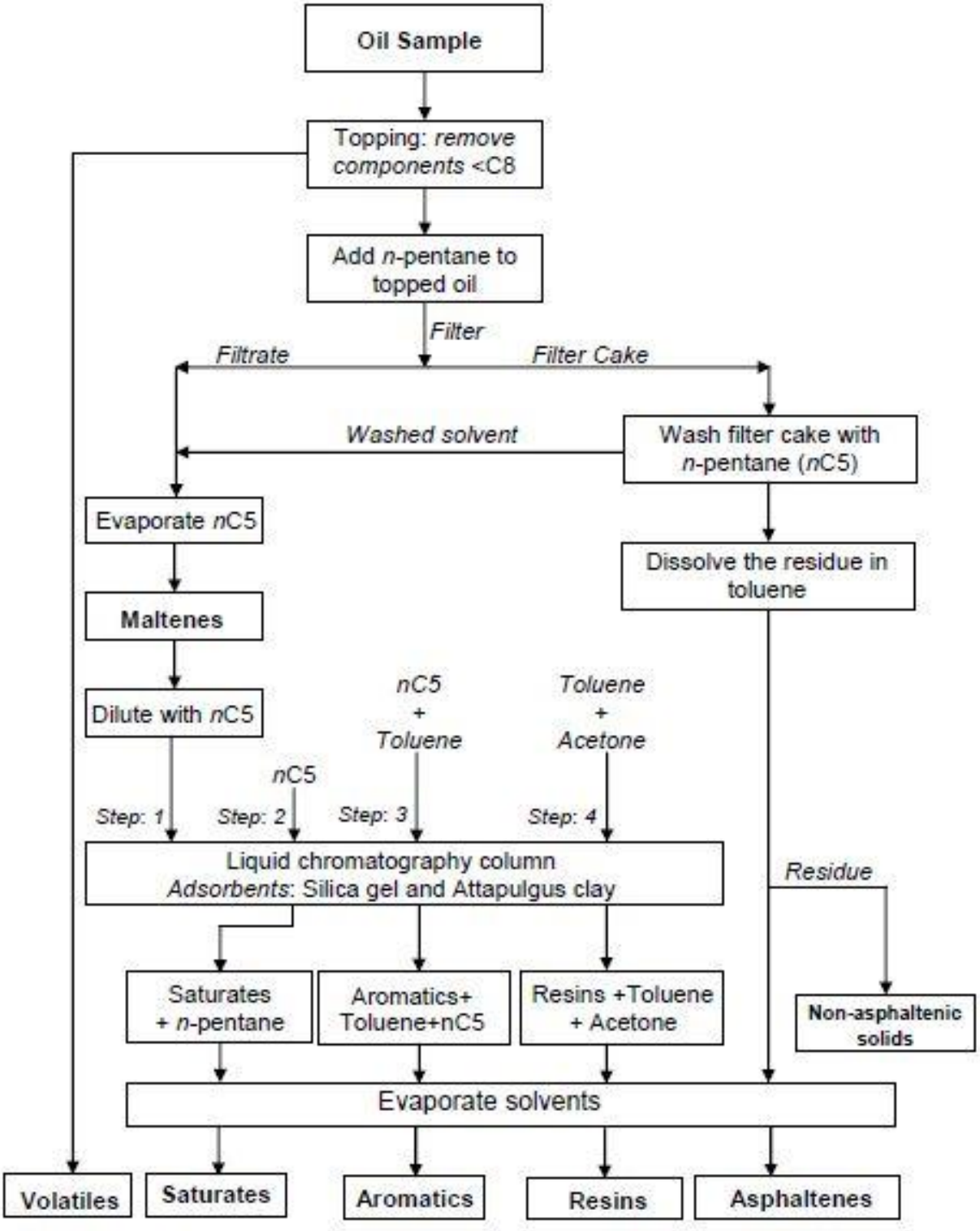

Figure 3: Flowchart of SARA fractionation method- University of Calgary procedure (Tharanivasan, 2012)

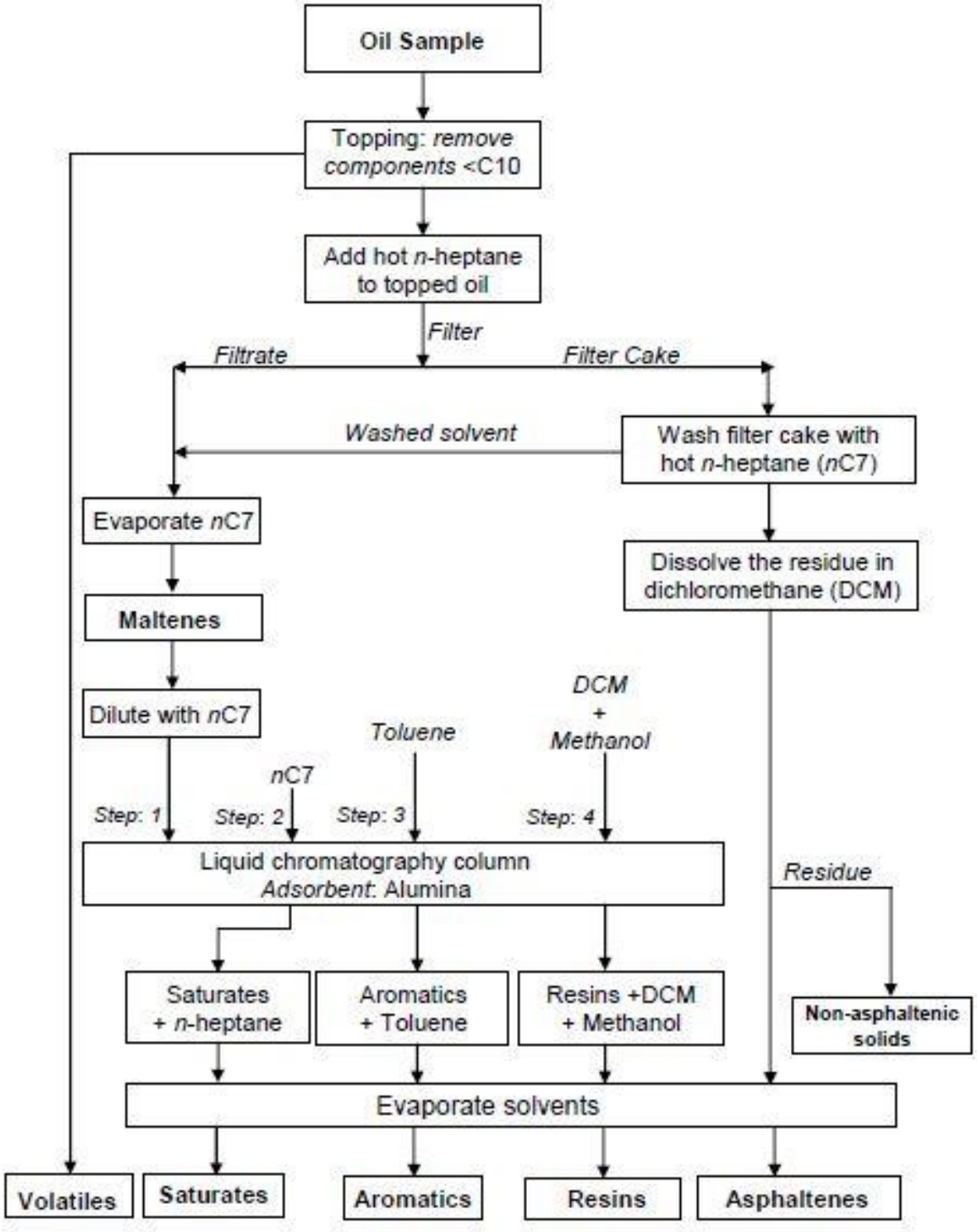

Figure 4: Flowchart of SARA fractionation method- DBR procedure (Tharanivasan, 2012)

Aske (2012) had developed HPLC system for SARA analysis which consist of HPLC-pump, two 7.8 x 300 mm μBondapak NH_2 columns in series, and an ultraviolet (UV) and a refractive index (RI) detector. The system is shown in figure 5. The first step of the process is to take out the asphaltene by n-hexane precipitation. The remaining of the oil is then diluted in n-hexane and injected onto the system through the injection valve ahead of the separation columns. Hexane is used as mobile phase. Saturates which have no retention on the column material, elutes first and are detected on the RI-detector. Both fractions are collected in separate vials after the detectors. The resins should be eluted with a more polar mobile phase. This can be done by reversing the flow through the columns by a backflush valve, and by using trichloromethane as mobile phase. Finally, the solvent is evaporated by all three collected fractions, and SARA distribution may be calculated by including the asphaltene yield.

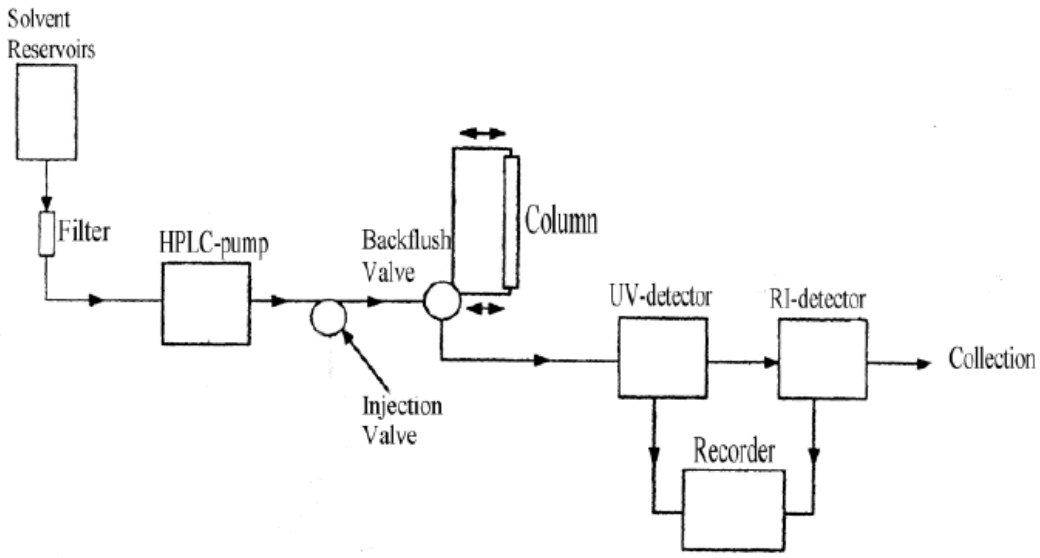

Figure 5: HPLC- System (Aske, 2012)

Colloidal instability index (CII) is one of the methods to analyse crude oil system with asphaltene deposit problems (Yen *et al.*, 2001; Choiri, 2010). It is the ratio of the total asphaltenes and saturates to the total of aromatics and resins as illustrated in figure 6. CII below 0.7 is considered as stable while CII higher than 0.9 is considered as unstable.

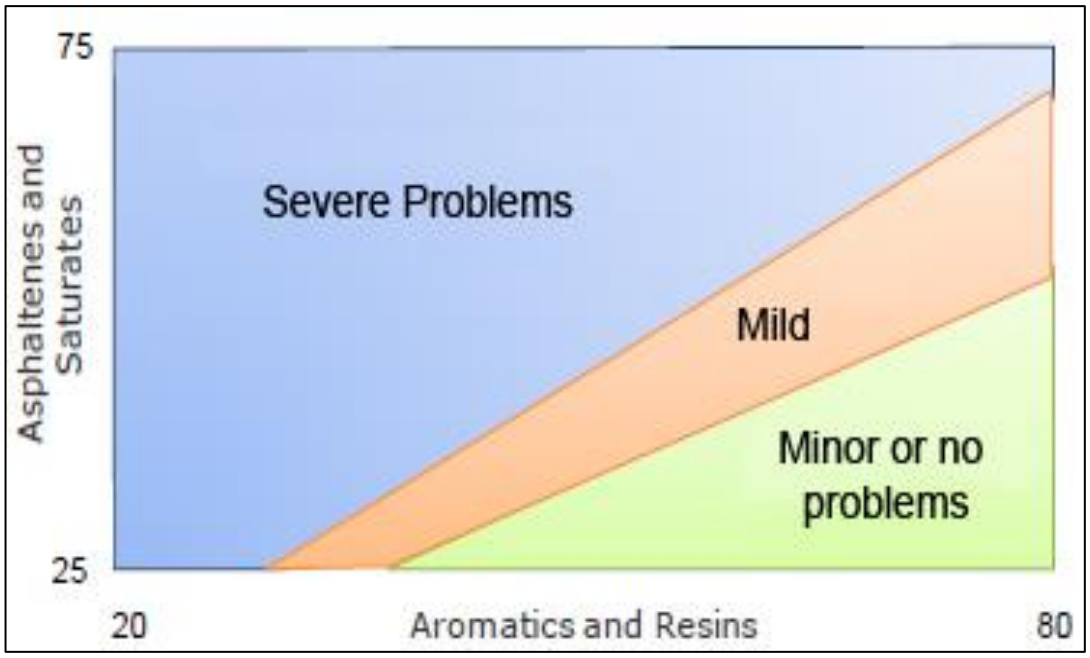

Figure 6: Colloidal instability index (Choiri, 2010)

2.5 Wax Content

Wax is an organic solid that appears as the temperature of the system drop. To quantify the amount of wax in crude oil, the sample has to be chilled to a very low temperature (e.g. -30 ^{o}C) before being filtered (Carnahan, 2007). UOP-46 method can be used to determine the wax content of crude oil (Vara & Gonzalez, 2011). This method involved dissolving a sample of deasphalted crude oil in petroleum ether as well as the addition of Fuller's earth to the solution. The mixture was then filtered and evaporated. Lastly, a mixture of one part of petroleum ether and three part of acetone was added to the solution which was chilled to -18^{o}C and filtered by a cold filter funnel, after which the sample was washed with hot petroleum ether which was evaporated to recover the wax. The results and findings are useful in designing a pipeline system.

2.6 Effect of temperature, pressure, water and carbon dioxide on the behaviour of waxy and asphaltenic crude oil

EOR method which is miscible-$C0_2$ flooding can cause asphaltenes to precipitate because the CO_2 may contact with oil and change the behaviour and equilibrium of the fluid (Choiri, 2010). Based on the research conducted by Mansoori (1999), it is stated that the higher the pressure, the greater the asphaltene deposits in live oil as in figure 7.

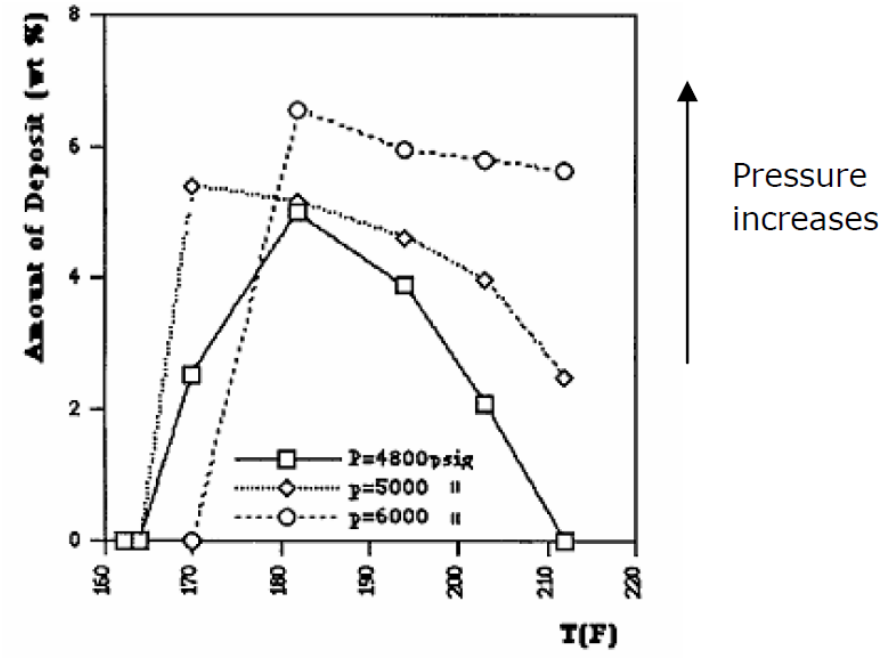

Figure 7: Trend of amount of asphaltene deposited as temperature and pressure changes (Mansoori, 1999)

Li (2010) reported that by using Daqing waxy crude oil sample with different water cut, an increase of pressure from 0.1Mpa to 12Mpa will increase the wax appearance temperature (WAT) and wax disappearance temperature (WDT) linearly. At constant pressure, WAT is always lower than WDT.

There are several experimental methods to analyst the problems of asphaltene deposit such as Gravimetric Method, Acoustic Resonance Technique Method (ART) and Light Scattering Method (LST) (Choiri, 2010). Gavimetric method relies on the selected pressure steps using PVT cell. The asphaltene will start to precipitate and fall to the bottom of PVT cell at the onset point. Therefore, choosing a small pressure steps is important for accurate result. The result will be illustrated on the plot of asphaltene concentration versus pressure.

ART method measures the changes in the acoustic fluid properties while asphaltene drops out from the solution. Acoustic receiver is used in the ART method to detect acoustic resonance which is emitted by an acoustic transducer. During depressurization, a sharp drop in acoustic responses is detected representing the upper Asphaltene onset pressure (AOP).Light scattering method or solids-detection system (SDS) uses near-infrared light to probe fluid as asphaltene precipitates either at isothermal depressurization or at isobaric with decreasing temperature. When the

asphaltene is precipitated, the light is scattered and the transmittance power of the light is reduced. The light's transmittance power is measured by fiber-optic sensors located at the other side of the cell. The result shows that when the pressure decreases, the light transmittance power increases due to denser fluid which gives more light transmission.

2.7 Wax appearance temperature (WAT)

Laboratory measurements of the cloud points are made on stock tank oil (STO) samples. It can be predicted from several empirical models and thermodynamic as well as from laboratory experiments such as Differential Scanning Calorimetry (DSC), Viscometry, Density, Filter Plugging, Cross-Polar Microscopy (CPM), Fourier Transform Infrared Spectrometry (FT-IR) and Nuclear Magnetic Resonance (NMR) techniques. DSC, CPM and Viscometry have been mostly used by researches (Ronningsen *et al.*, 1991; Hamouda *et al.*, 1993; Calange *et al.*, 1997; Pan *et al.*, 1997; Cazaux *et al.*, 1998; Elsharkawy *et al.*, 1999; Thomason, 2000;; Chen *et al.*, 2004; Alboudwarej *et al.*, 2006; Bordalo *et al.*, 2007; Ekweribe *et al*., 2008; Vara & Gonzalez, 2011).

The ASTM D2500-88 method relies on visual observation of the wax crystals. Therefore, it requires the sample to be transparent in layers about 30 mm in thickness and the method is not suitable for dark crude oil (e.g. black oil). WAT are usually determined by using DSC, CPM, Light Transmittance (LT) or viscometry for black oil. DSC, LT and viscometry techniques require that sufficient paraffin crystallize before the properties of the crude oil change enough for the liquid/solid (L/S) phase transition to be detected. The limit of detection of DSC and LT techniques is larger and WAT values from these techniques will lay further inside the solid-liquid phase envelop. For low wax content crude oil, WAT may go completely undetected by viscometry, DSC and LT. The CPM is generally deemed to be the most sensitive and the only direct visual technique applicable for all non-biodefraded oil including opaque fluids (Hammami *et al*., 1999).

2.7.1 Differential Scanning Calorimetry

The Differential Scanning Calorimetry (DSC) measures the difference in the heat released (or absorbed) between test sample and a reference heated to 80^{o}C and

cooled at a specific cooling rate. The reference should be thermally inert and stable over the temperature range and with known properties. During cooling period, the test sample at WAT starts to cool slower than the reference due to the release of heat of crystallization which will be captured by an analyzer. This point is seen as a deviation from the straight line trend above the WAT measure on the thermogram as in figure 8. The weight fraction of crystallized wax can be measured if the enthalpy of fusion of a sample is determined. This solid weight fraction as a function of temperature defines the solubility curve for crude oil.

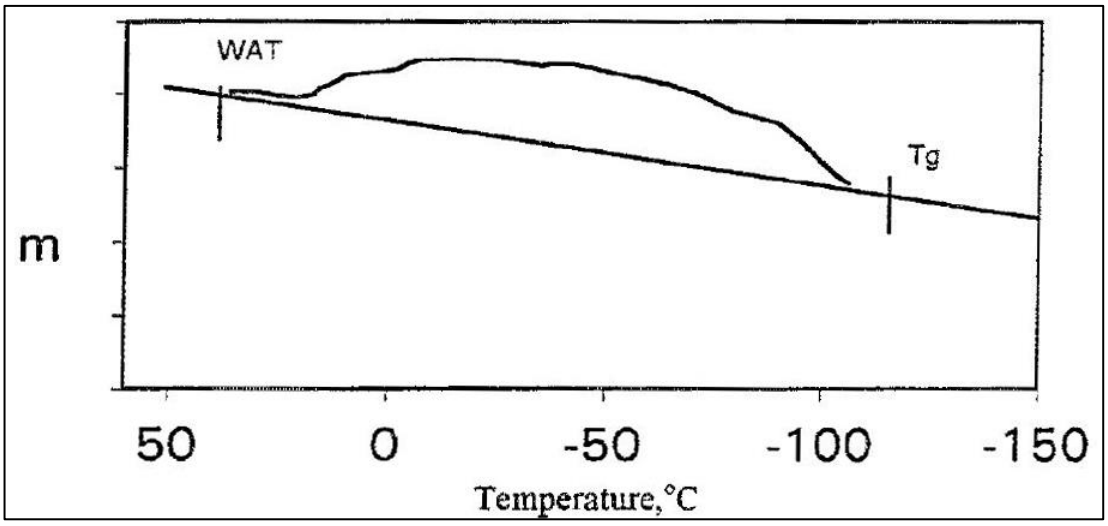

Figure 8: DSC thermogram of Kuwait crude oil during cooling (Elsharkawy *et al*, 1999)

2.7.2 Cross Polar Microscopy

The Cross Polar Microscope (CPM) is based on the property of wax crystals to rotate the polarization plane of linearly polarized light. There are two type of polarizers used in the CPM: the first forces light to undulate in only one direction while the second placed at 90^{o}C from the first, totally blocks the light wave. When the sample is cooled on a cooling stage of the microscope, wax crystals form which can rotate the polarization plan of light i.e. light will be transmitted as paraffin crystals form. The first white dot will appear as the temperature reaches the wax appearance temperature of the sample as in figure 9.

Figure 9: Stock tank oil at 70^{o}F (WAT at 103.6^{o}F) (Jamaluddin *et al*. 2001)

2.7.3 Viscometry

Rheological properties of crude oil will change as wax precipitates hence making viscometry method possible for WAT measurement (Ronningsen *et al*., 1991). Pan *et al*. (1997) studied wax precipitation using four oil samples. During the experiment, the sample was cooled at specified rate and measurements were taken at testing temperature down to equilibrium temperature. The process was repeated for lower temperatures until WAT was established. Several researchers studied this approach and successfully measured the WAT of crude oil by plotting the logarithm of viscosity (μ) against the inverse of temperature (*1/T*) (Ronningson *et al*., 1991; Giordani, 1993; Bordalo *et al*., 2007).

CHAPTER THREE

METHODOLOGY

3.1 Research Methodology

The methodology for this research project is based on experiment and analysis. The results obtained from this research are used to compare with other literature results for different methods and samples.

3.1.1 Sample Preparation

The samples were obtained from Petronas Penapisan (Melaka) Sdn Bhd which comes from different field, namely: Tapis, Dubai, Arab, Miri and Dulang. The crude oil received is in large volume which around two to three litre so they are heated to 80^{o}C for 8 hours in water bath to prevent separation of light crudes and heavy crudes as well as to eliminate the thermal history which can affect the results. During the heating process, the crude oils are stirred from time to time for complete homogeneity and dissolution. After that, the samples are immediately transferred to smaller container as shown in figure 10. This procedure reduces the time taken for pre-heating before each experiment to one to two hour as smaller volume is involved.

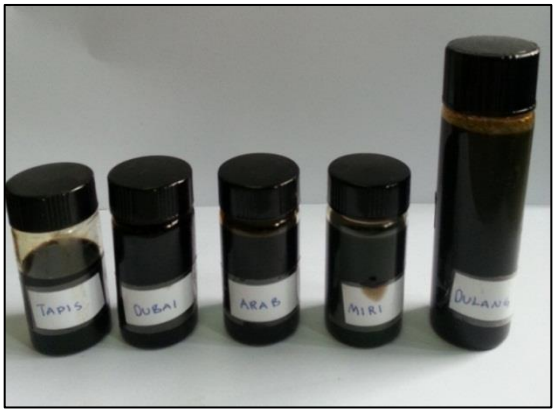

Figure 10: Crude oil samples

3.1.2 Gas Chromatography Mass Spectrometry (GCMS)

For the project, Agilent 5975C/7890A Gas Chromatography Mass Spectrometry is used to determine the sample's carbon distribution as in figure 11. Inner diameter of 0.32 millimetres, phase thickness of 0.25 millimetres and DB-5 capillary column of 30 meters is used for the experiment. Helium is used as carrier gas.

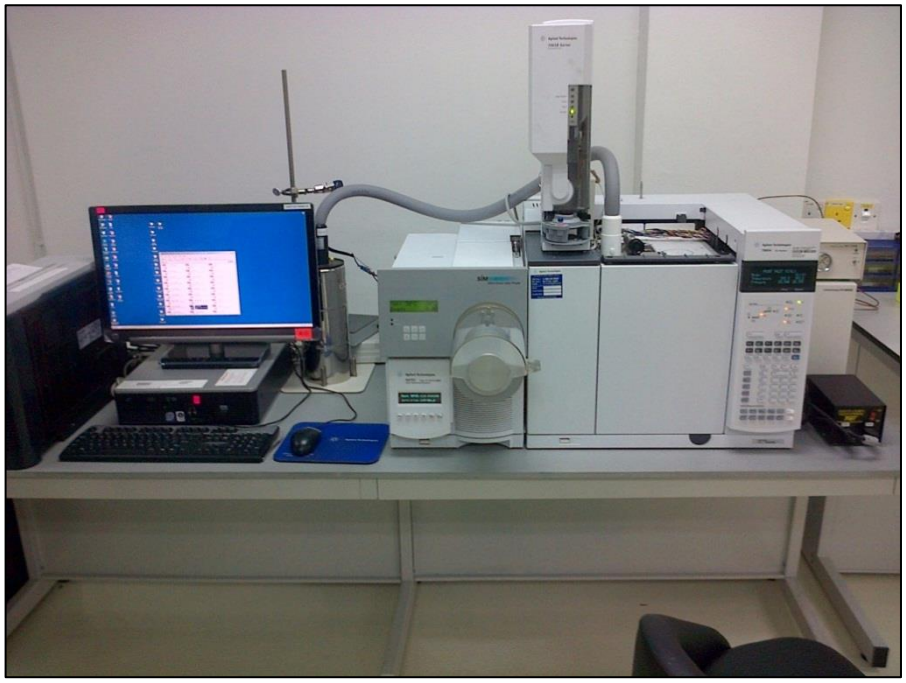

Figure 11: Agilent 5975C/7890A Gas Chromatography Mass Spectrometry

Below are the lists of procedures for the experiment:

1) The temperature of oven is set at 120^{o}C and hold for 3 minutes. Then, the temperature is increased to 270^{o}C and hold for 40 minutes. Temperature increase rate set at 10^{o}C/min.
2) Splitless injection is carried when the temperature reaches 300^{o}C.
3) Constant flow rate mode is set at 2cm^{3}/min.
4) Mass Spectrometry (MS) transfer line is set at 300^{o}C.
5) Ion source is set at 230^{o}C and kept constant.
6) Procedures 1 to 5 are repeated by using different crude oil samples.

3.1.3 Differential Scanning Calorimetry (DSC)

Setaram Micro DSC7 Evo is used to determine the wax appearance temperature for this project. It allows the experiment to be run from sub-ambient temperature of -45^{o}C up to 120^{o}C and under high pressure up to 400 bars. Figure 12 shows the setup for DSC which consist of gas bottle, high pressure gas panel and Micro DSC7 Evo equipped with high pressure cell.

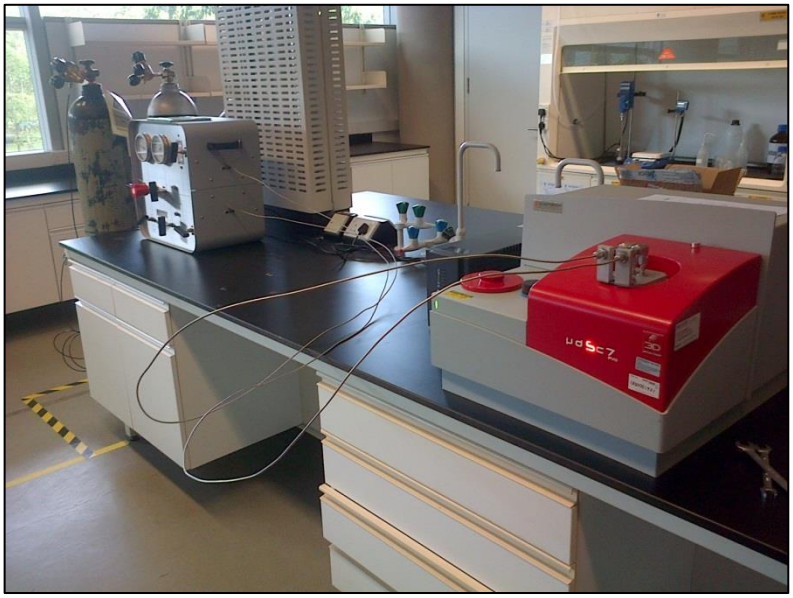

Figure 12: Micro DSC7 Evo system

Below are the lists of procedures for the experiment:

1) Around 50 mg of each sample is prepared and put into DSC for analysis
2) The samples are heated for from 20^{o}C to 70^{o}C and hold for 3 minute to achieve stable state
3) The samples are cooled to -20^{o}C.
4) The samples are heated back to 70^{o}C.
5) The heating and cooling rate is 2^{o}C/min.

3.1.4 Wax content

UOP (Universal Oil Product) 46-85 method is used to determine the wax content of crude oil samples. The procedures of the experiment are listed as below:

1) Crude oil are dissolved in hexane and stirred continuously on a hot plate.

2) Sulphuric acid (H_2SO_4) is added to the solution to produce an acidic tar with the asphaltene.
3) The oil-paraffin solution is poured into a separator funnel and the asphaltene product is washed for a few times in hexane.
4) Water is added to dilute the concentrated acid. Aqueous layer is then removed upon separation.
5) Ammonium hydroxide and water washes are used and repeated for several times to neutralize the sulphuric acid. Neutrality which indicated by colour change is checked by an aqueous phenolphthalein solution.
6) Hexane-wax solution is moved to a flask and reduced by evaporation before being re-dissolved in warm methylene chloride ($MeCl_2$).
7) Dry ice is used to cool $MeCl_2$ to -30^{o}C to make sure that complete precipitation of wax is achieved in the solution.
8) The solution is then filtered under vacuum and the flask is rinsed with a series of chilled $MeCl_2$.
9) The filter which contains wax is dissolved with warm hexane and collected in tarred flask before being evaporated.
10) Wax is weighted and the wax content is calculated.

3.1.5 Density Measurement

Portable density meter ($DMA32_N$) is used for this project to find the density of the sample at temperature of 26.5 ^{o}C as in the figure 13.

Figure 13: Portable density meter ($DMA35_N$)

The procedures are as follows (ASTM D7777):

1) The samples are poured into the beaker.
2) The lever of the pump is pushed down and the filling tube is submerged in the sample.
3) The pump lever is slowly released and the reading is recorded.
4) The procedures are repeated for each sample of crude oil.

3.1.6 Density Meter

Anton Paar DMA 5000M density meter is used to determine the density of the sample as in figure 14. The equipment is setup for a temperature scan by cooling the samples from 50^{o}C to 0^{o}C at atmospheric pressure. Temperature step of 2^{o}C was selected. The measurements by Anton Paar density meter are carried out according to ASTM Standard D5002-99. The density meter gives fast, reliable and accurate measurement as well as requires only small amount of sample.

Figure 14: Anton Paar DMA5000M density meter

3.1.7 SARA Analysis

Sara analysis is divided into two stages. The first stage is to collect and remove asphaltene from the sample using ASTM D3279. The procedures for asphaltene separation is as listed below:

1) 1 gram of crude oil and 100 ml of n-heptane is inserted into 250 ml 2-neck round bottom flask.
2) The solution is gently stir for 20 minutes using magnetic stirrer and secured under the reflux condenser as in figure 15.
3) The Gooch crucible plus one thickness of the glass-fiber filter pad is placed in an oven at 107^{o}C for 15 minutes and it is then placed in desiccator for cooling for 15 minutes.
4) The Gooch crucible plus one thickness of the glass-fiber filter pad is then weighted to the nearest 0.1mg. It is then set up in the suction flask.
5) The content of the flask (50^{o}C) is poured through the filter using a gentle vacuum. The setup is as in figure 16.
6) The precipitate is washed with three portions of n-heptane of 10ml each.
7) Finally, the crucible plus filter pad along with asphaltene is placed in the oven at 107^{o}C for 15 minutes before being cooled down and weighted.

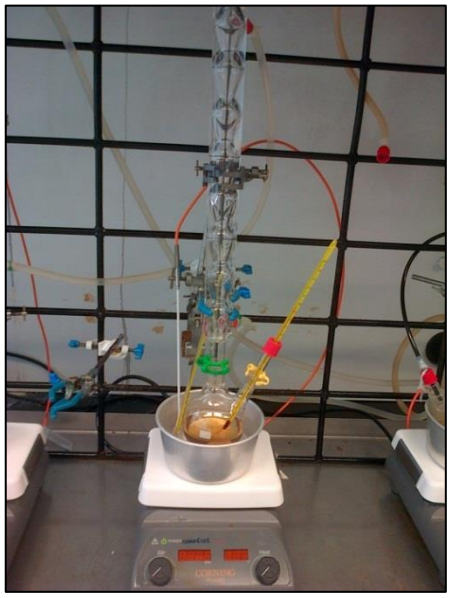

Figure 15: Solution is stirred under reflex condenser

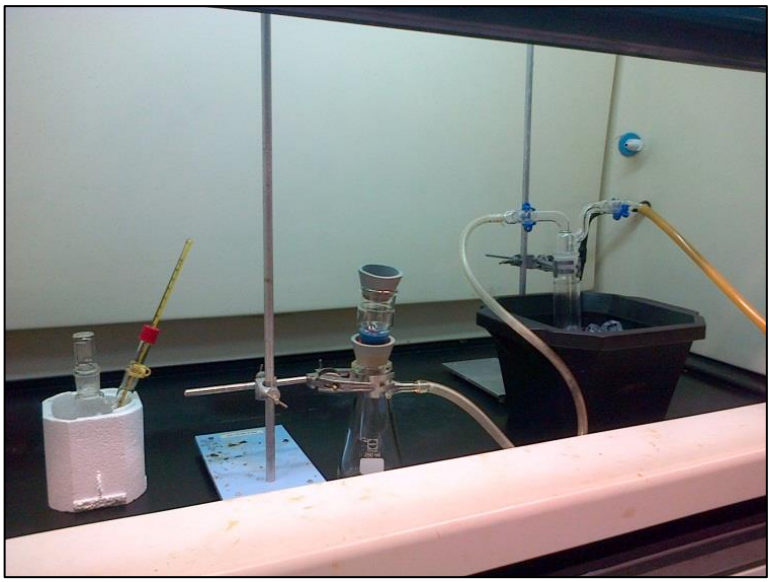

Figure 16: Experiment setup to filter the asphaltene

Then the de-asphalted crude oil (maltenes) is isolated to saturates, aromatics and resins using Agilent 1260 Infinity HPLC as in figure 17. The HPLC unit is setup using Volatile Organic Compounds (VOC) standards provided by Agilent for various conditions. The mixture comprises of 100µg mL^{-1} each of n-pentadecane, n-decane, n-octadecane, n-tridecane, toluene, 1-methylnaphthalene, 1,3 diisopropylbenzene and phenanthrene dissolved in n-pentane. Two 9.4x250mm Zorbax NH_2 columns with 5 µm packing is used in series with a UV detector operating at a wavelength of 254 mm as suggested by Mansoori *et al*. (2007).

Dichloromethane (DCM), n-hexane, and iso-propanol (IPA) is used as a solvents. The de-asphalted crude oil is filtered using a 0.2 µm PTFE syringe filter into 1.5 glass vial. Saturates and aromatics are firstly eluted and dichloromethane is used to extract the resins which are retained in the column during HPLC separation. The Rotavapor is used to extract the resins as in figure 18. The system is flushed and cleaned for the next analysis by flushing with iso-propanol and n-hexane for 15 min.

Figure 17: High pressure liquid chromatography (Agilent 1260 Infinity)

Figure 18: Resin separation using rotavapor

3.2 Project Activities

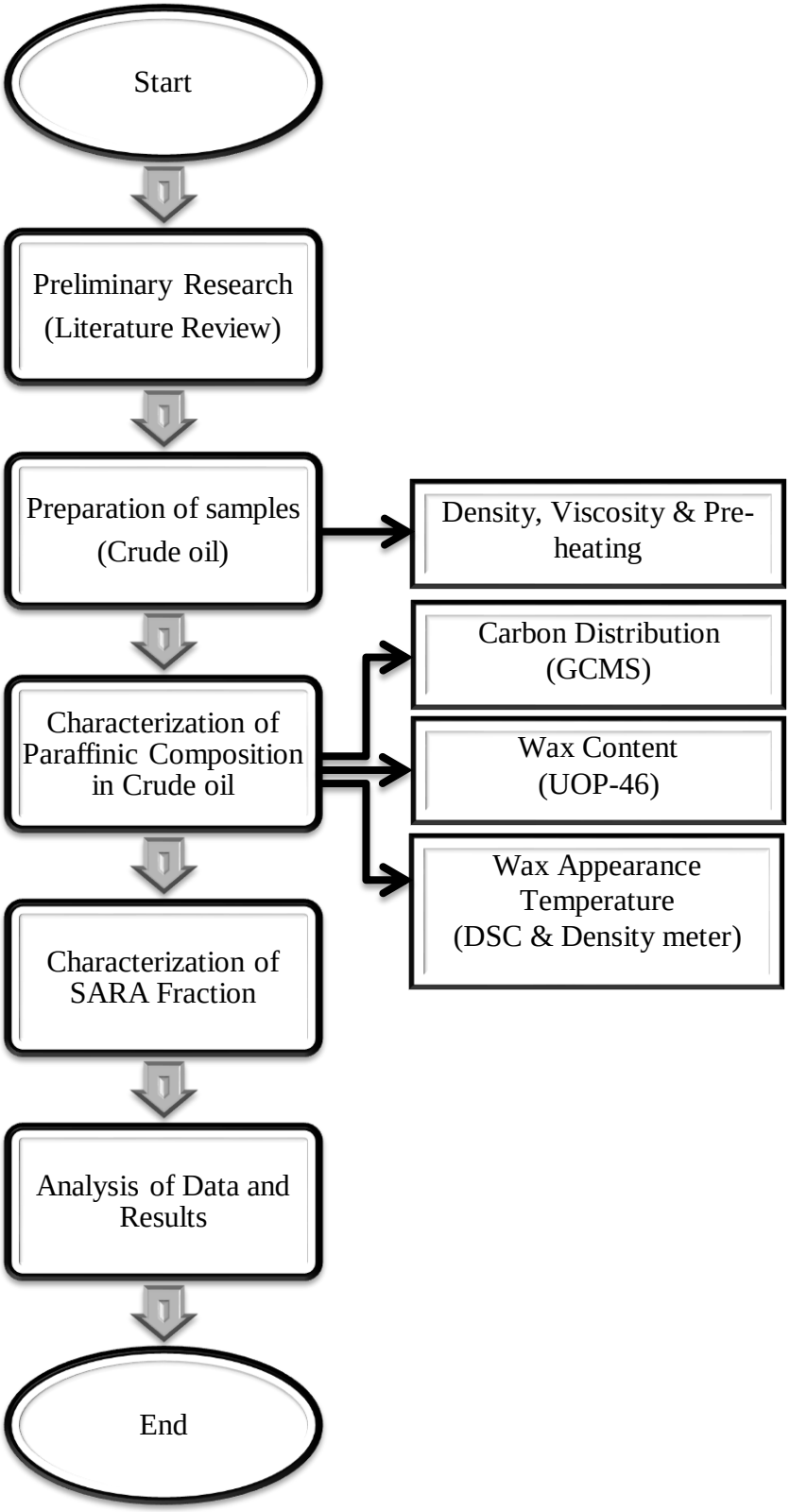

Figure 19: Project activities

3.3 Key Milestone

Several key milestones for this research project must be achieved in order to meet the objective of this project. Figure 20 shows the key milestones that need to be achieved by the author throughout the period of the research which is about 8 month.

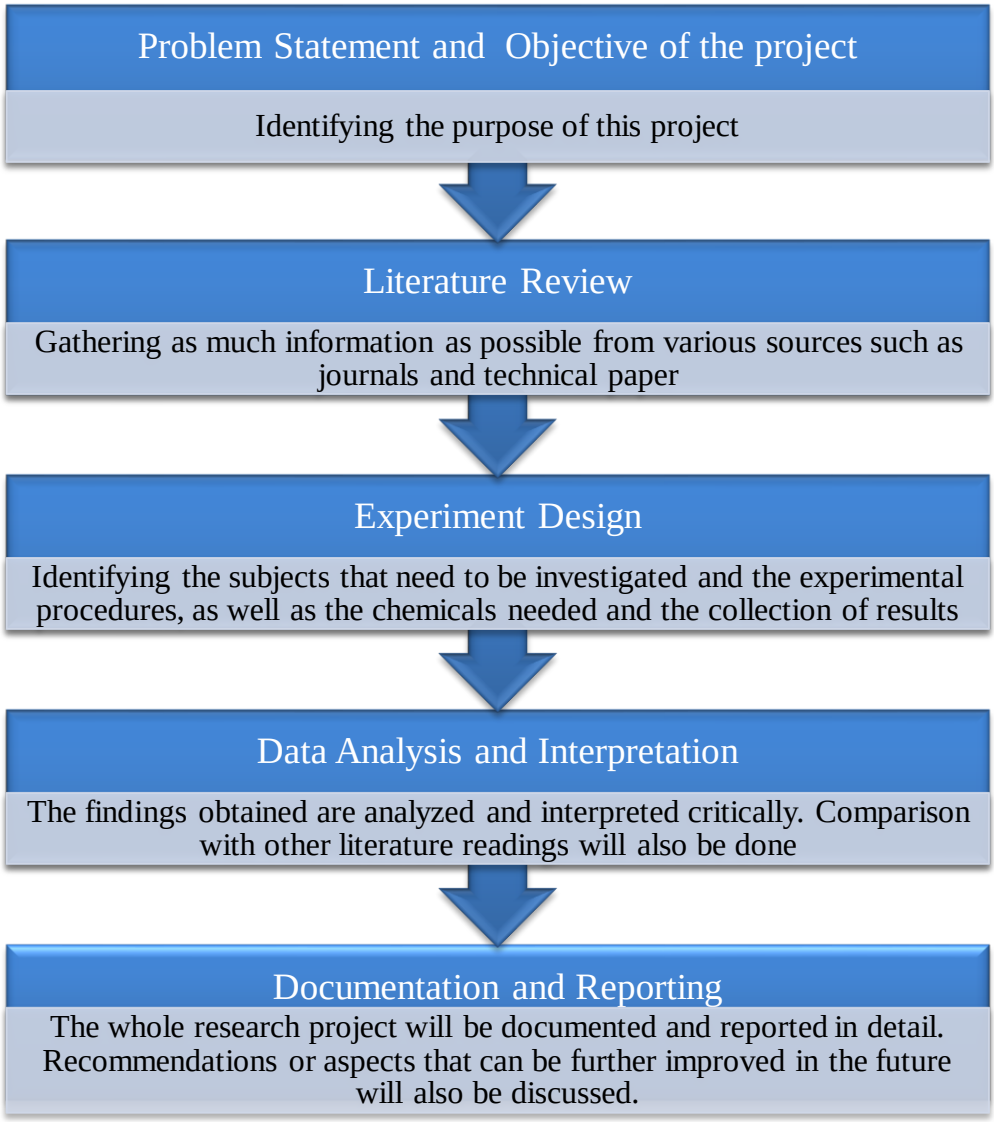

Figure 20: Key milestone

3.4 Gantt-Chart

	Final Year Project 1														Final Year Project 2													
Task	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Topic selection																													
Prelim Research																													
Collecting reference																													
Preparation for extended proposal																													
Submission of extended proposal																													
Prepare methodology																													
Proposal defence																													
Prepare the equipment to be used																													
Preliminary results																													
Preparation for Interim Report																													
Submission of Interim Draft Report																													
Submission of Interim Report																													
Start the experiment																													
Analyse the result																													
Verify the result with other journal																													
Preparation for progress report																													
Submission of progress report																													
Pre-EDX																													
Preparation for Final Report																													
Preparation for Technical Paper																													
Submission of Draft Report																													
Submission of Soft Bound																													
Submission of Technical Paper																													
Preparation for Oral Presentation																													
Oral Presentation																													
Submission of Hard Bound																													

Figure 21: Gantt-chart

	Process
	Key Milestone

CHAPTER FOUR

RESULT AND DISCUSSION

The results obtained from various experiments are presented and analysed in this chapter.

4.1 Density

Density of all samples has been tested at normal laboratory temperature which is 26.5^{o}C and converted into ^{o}API density using Equation 1. The result is tabulated in Table 4.

$$°API = \frac{141.5}{sg} - 131.5 \qquad [1]$$

Table 4: Density measurement at 26.5^{o}C

Sample	Density	^{o}API
Dulang	0.837 g/cm^3	37.60
Tapis	0.828g/cm^3	39.39
Miri	0.869g/cm^3	31.33
Dubai	0.871g/cm^3	30.95
Arab	0.862g/cm^3	32.65

According to the table, we can observe that the density of Dubai crude oil is the highest while the density of Tapis Crude oil is the lowest. The calculated ^{o}API density shows that all of the samples are categorized as light oil.

4.2 SARA Fraction

The SARA fractions measured for Dulang, Arab, Tapis, Miri and Dubai is summarized in Table 5. Colloidal Instability Index (CII) is calculated by using Equation 2.

$$CII = \frac{Saturate + Asphaltene}{Resin + Aromatic} \qquad [2]$$

Table 5: SARA fractions of crude oil

Samples	Saturates (wt%)	Aromatics (wt%)	Resins (wt%)	Asphaltenes (wt%)	Colloidal Instability Index
Dulang	82.15	17.85	2.26	0.18	4.09
Arab	51.36	38.16	7.15	3.33	1.21
Tapis	84.92	15.09	1.75	0.13	5.05
Miri	52.34	47.66	34.42	0.12	0.64
Dubai	57.22	42.78	20.83	0.34	0.90

From the table, we can see that Tapis has the highest CII value followed by Dulang, Arab, Dubai and Miri. Basically, the weight percentage of resins and asphaltenes is obtained through their weight after being filtered out while the weight percentage of saturates and aromatics is obtained through the refractive index which is compared to the standard. Refer to figure 35, figure 36, figure 37, figure 38 and figure 39 in appendix for the refractive index signal which indicates the ratio of saturates and aromatics in the samples.

It is observed that the weight percentage of asphaltene in Arab crude oil is high, but the average value of CII is 1.21 while Tapis crude oil with low asphaltene content has higher CII value which is 5.05. All samples have CII value higher than 0.9 except Miri and this indicates higher tendencies towards asphaltene deposition (Yen *et al.*, 2001 and Choiri, 2010). It means that crude oil possessing low asphaltenes content can also have higher tendency for precipitation as compared to those with higher asphaltene content and vice versa.

4.3 Gas Chromatography Mass Spectrometry

The purpose for GCMS is to analyse the hydrocarbon number distribution of the paraffinic composition in the 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 Y-axis of the chromatogram represents the abundance while the X-axis represents the retention time. The lighter components are more towards the left of the chromatogram while the heavier components are more towards the right of the chromatogram. The chromatograms are shown in figure 22, figure 23, figure 24 and figure 25 for Dulang, Tapis, Dubai and Arab respectively.

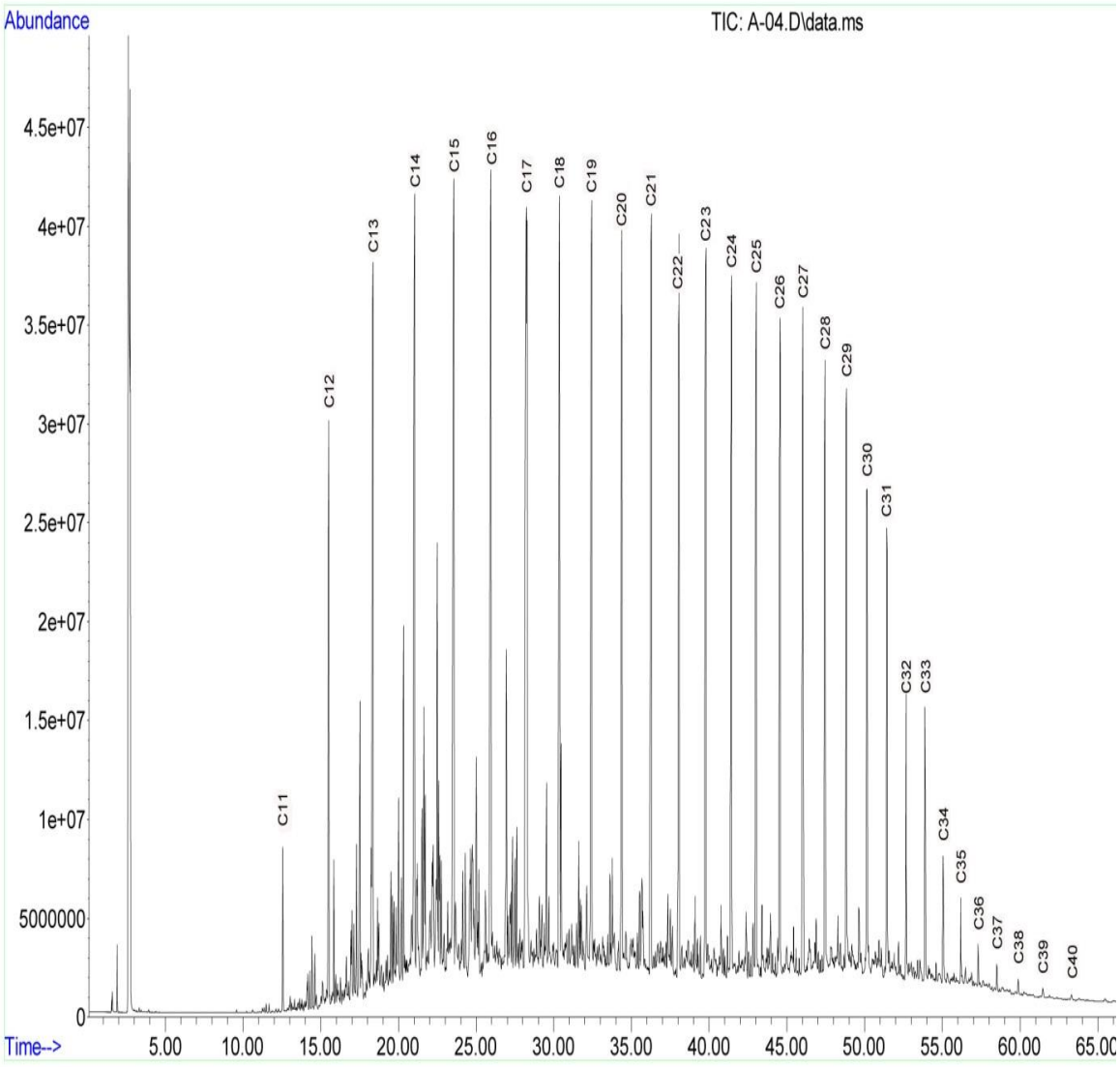

Figure 22: Chromatogram for Dulang crude oil sample

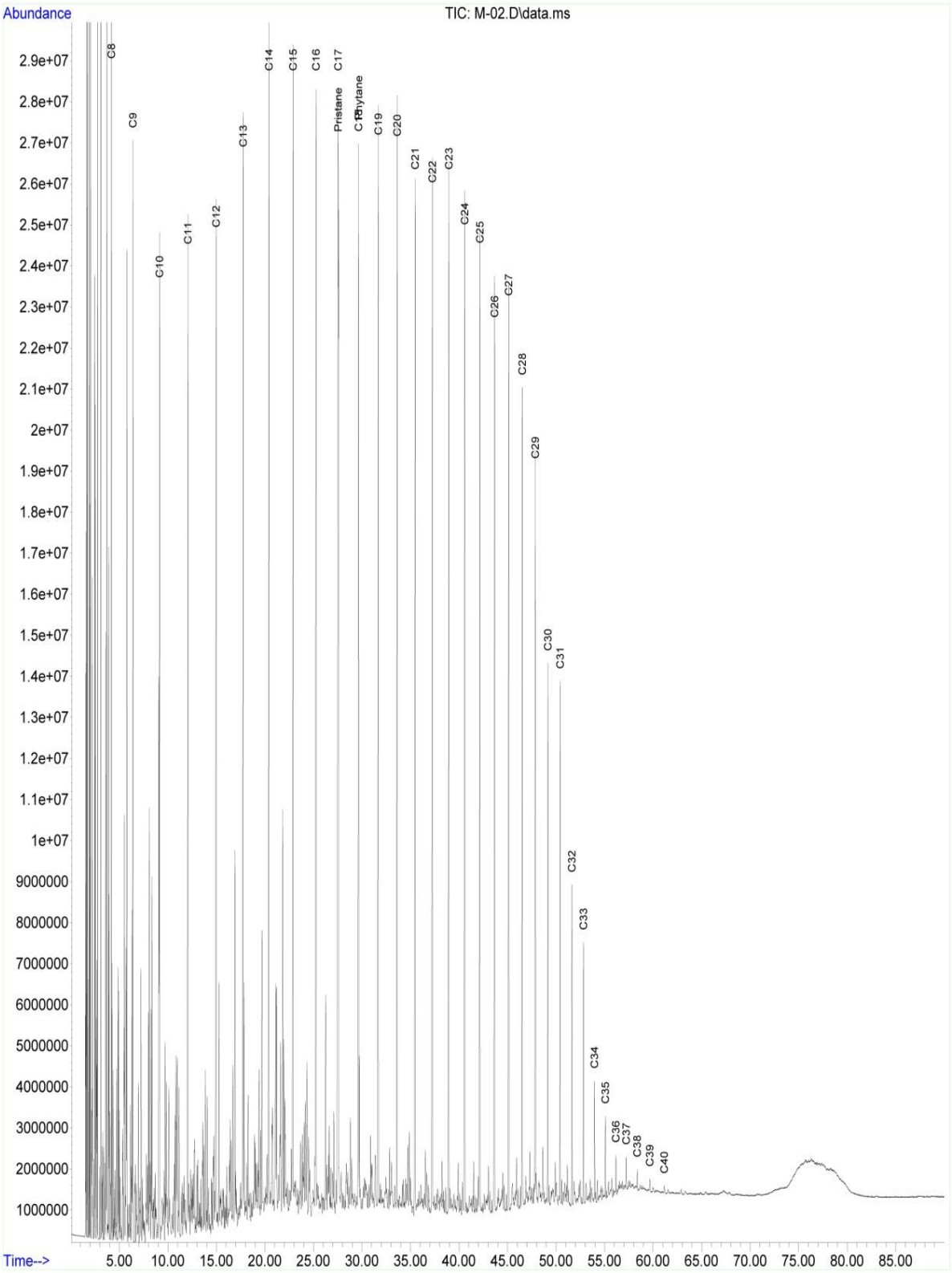

Figure 23: Chromatogram for Tapis crude oil sample

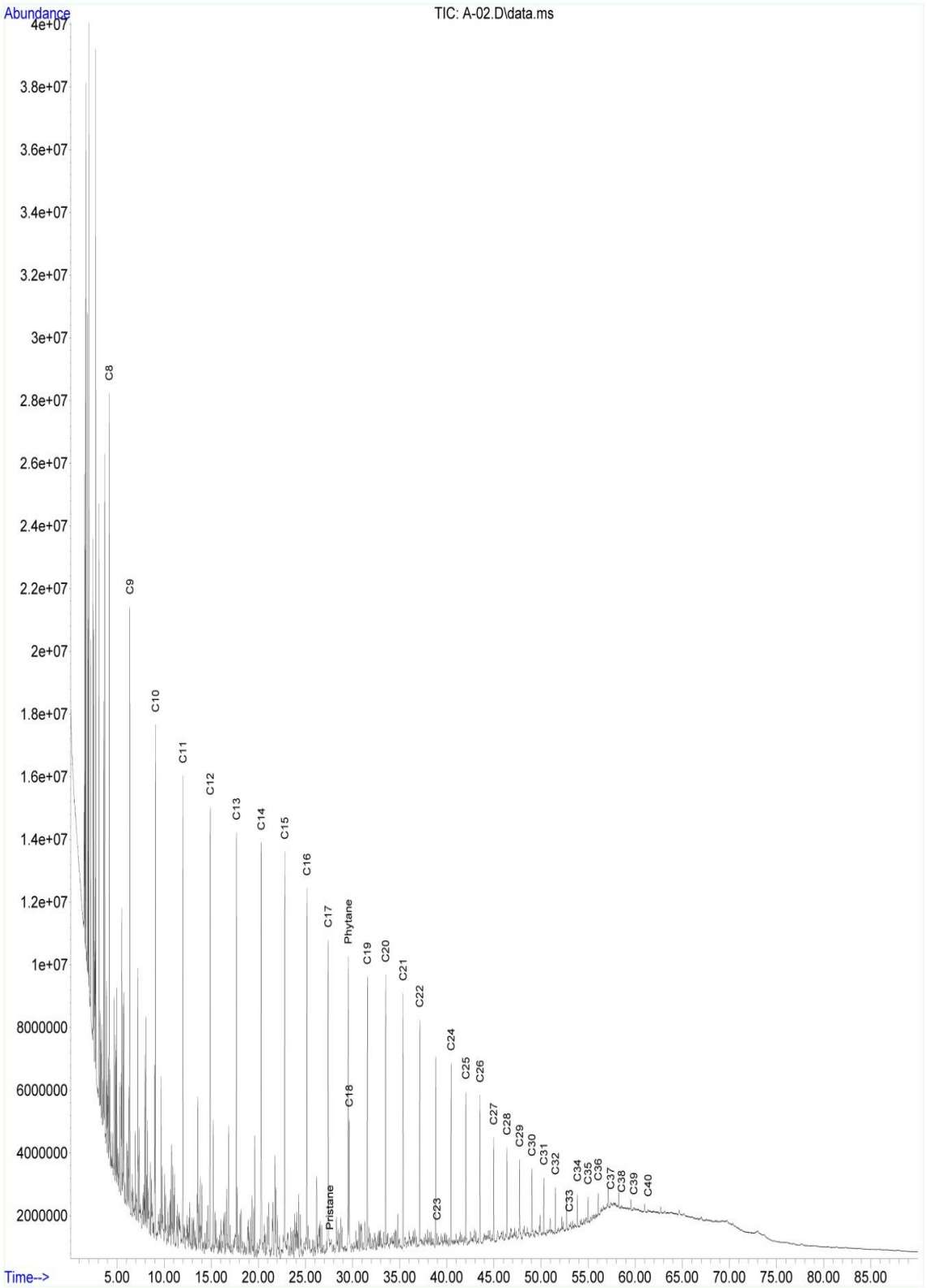

Figure 24: Chromatogram for Dubai crude oil sample

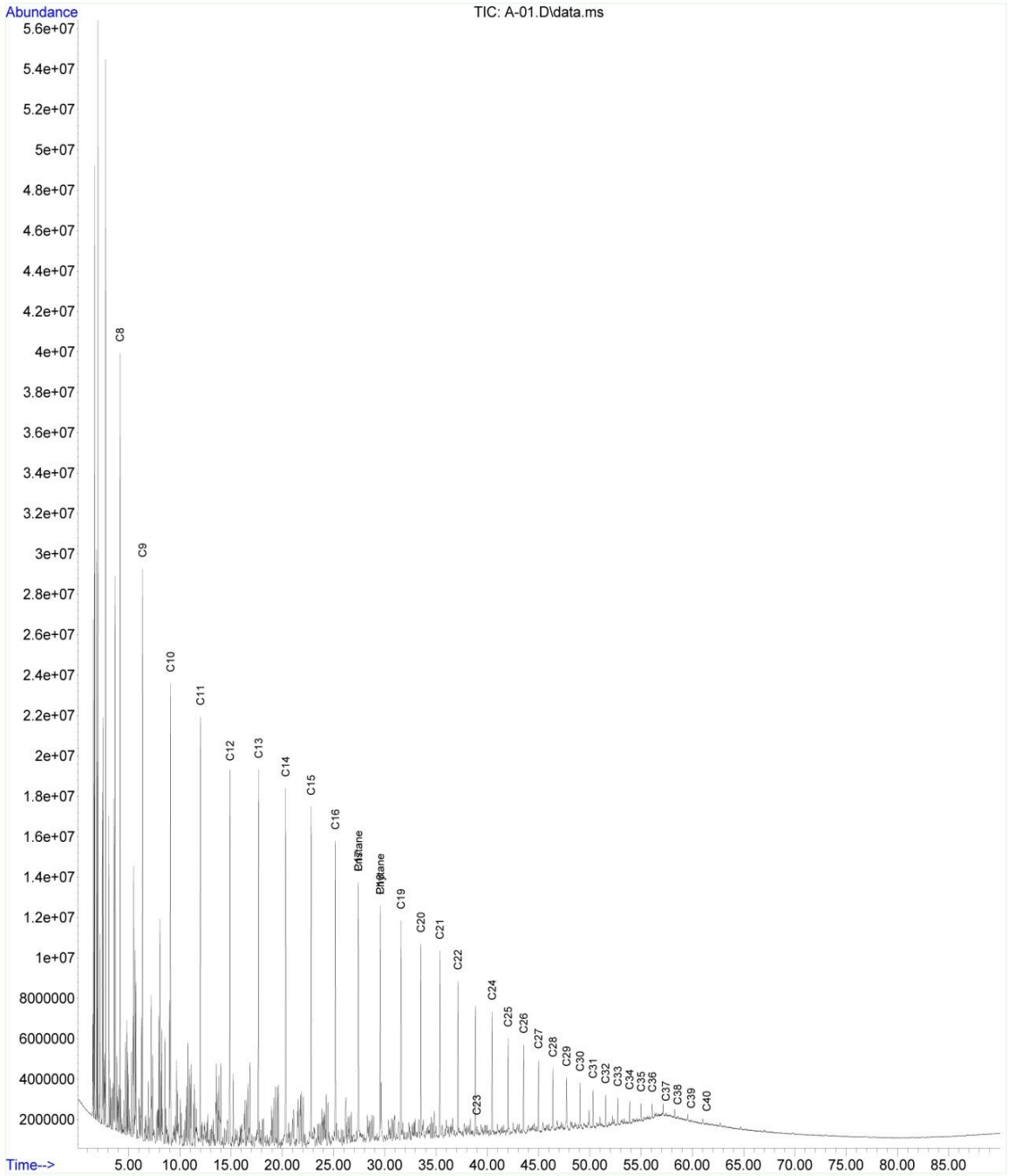

Figure 25: Chromatogram for Arab crude oil sample

The total area percent (area %) for carbon number range from C_{20} to C_{40} was tabulated in Table 6. Refer to Table 9 to Table 12 in appendix for the list of Carbon number with respect to retention time and area percent. It is observed that Dulang crude oil has the highest total area percent followed by Tapis, Arab and Dubai.

Table 6: Total area percent (C_{20} - C_{40})

Samples	Dulang	Tapis	Dubai	Arab
Total Area Percent	24.599 %	24.291 %	8.514 %	8.017 %

4.4 Wax Analysis

Wax appearance temperature (WAT) of crude oil samples wax measured by using DSC and density meter while the wax content was measured using UOP-46 method. Figure 26, figure 27, figure 28 and figure 29 shows the graph of heat flow against furnace temperature obtained from DSC for Dulang, Tapis, Miri and Dubai respectively. It represents the cool down portion of the heat flow curve. The wax appearance temperature is denoted by the section of the curve where the heat flow begins to decrease as the oil sample gives off heat energy.

Each experiment is repeated with different weight of sample and the result shows that the value of WAT is almost constant as in Table 7. Therefore, it can be conclude that the weight of sample does not affect the measurement of WAT.

Table 7: Wax appearance temperature

Sample	Weight (mg)	WAT (^{o}C)(DSC)	WAT (^{o}C) (Density meter)
Dulang #1	60	37.52	37
Dulang #2	79	36.97	-
Dulang #3	118	36.99	-
Tapis #1	52	26.36	25
Tapis #2	61	26.69	-
Tapis #3	130	26.86	-
Miri #1	65	12.34	12
Miri #2	75	12.30	-
Miri #3	101	12.44	-
Dubai #1	49	15.62	-
Dubai #2	81	15.41	-
Dubai #3	126	15.88	-

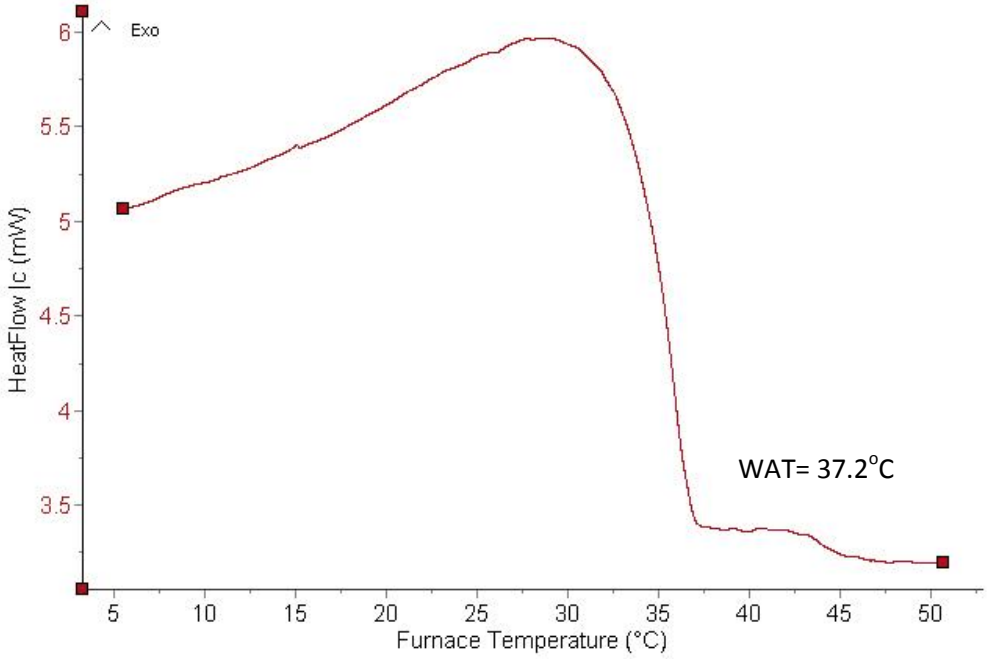

Figure 26: Graph of heat flow against furnace temperature for Dulang crude oil sample

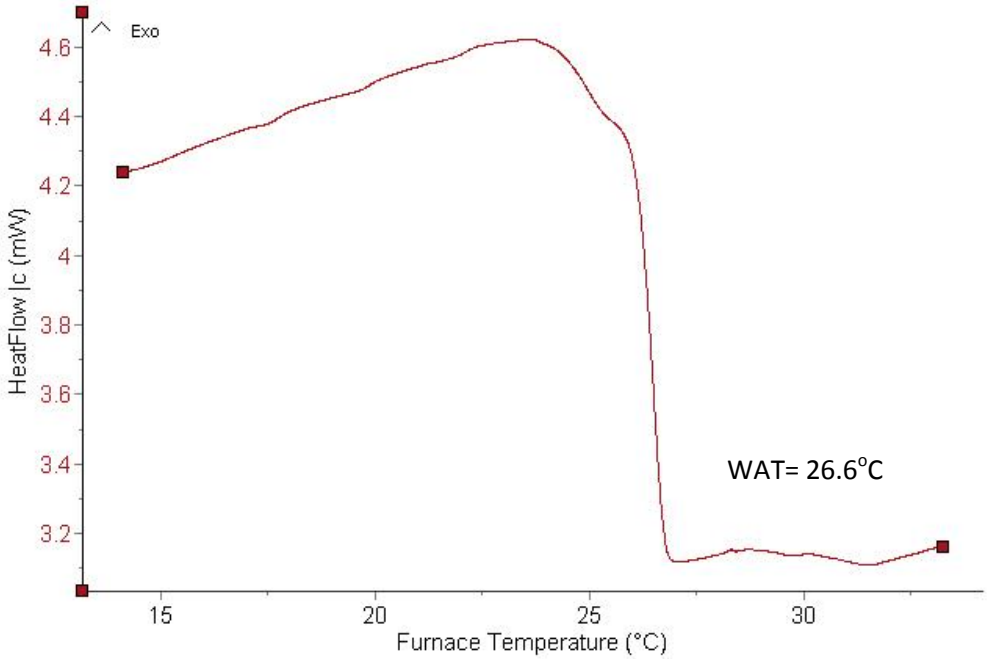

Figure 27: Graph of heat flow against furnace temperature for Tapis crude oil sample

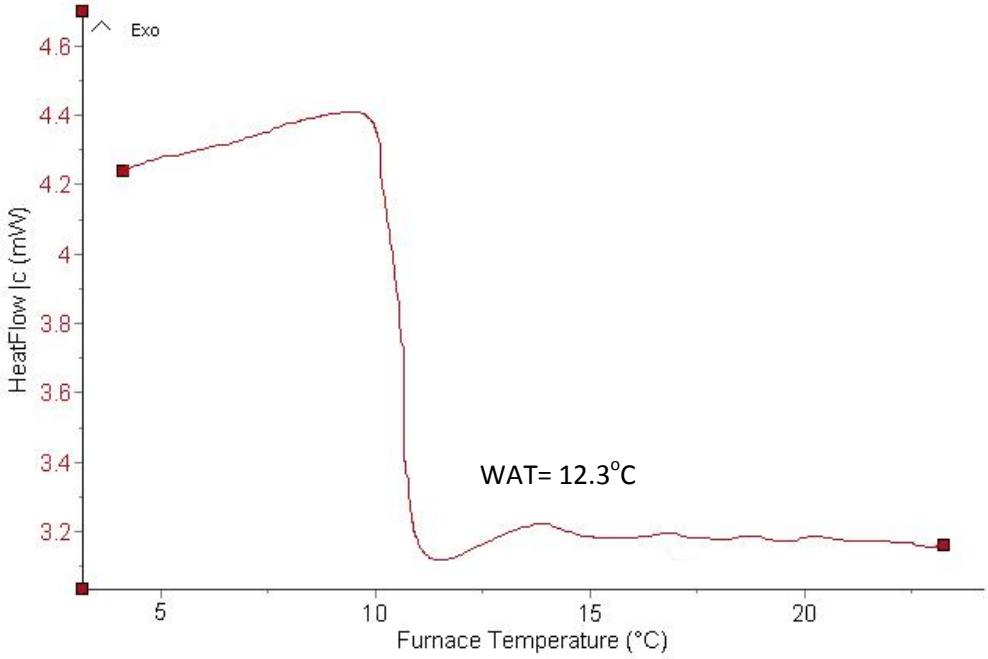

Figure 28: Graph of heat flow against furnace temperature for Miri crude oil sample

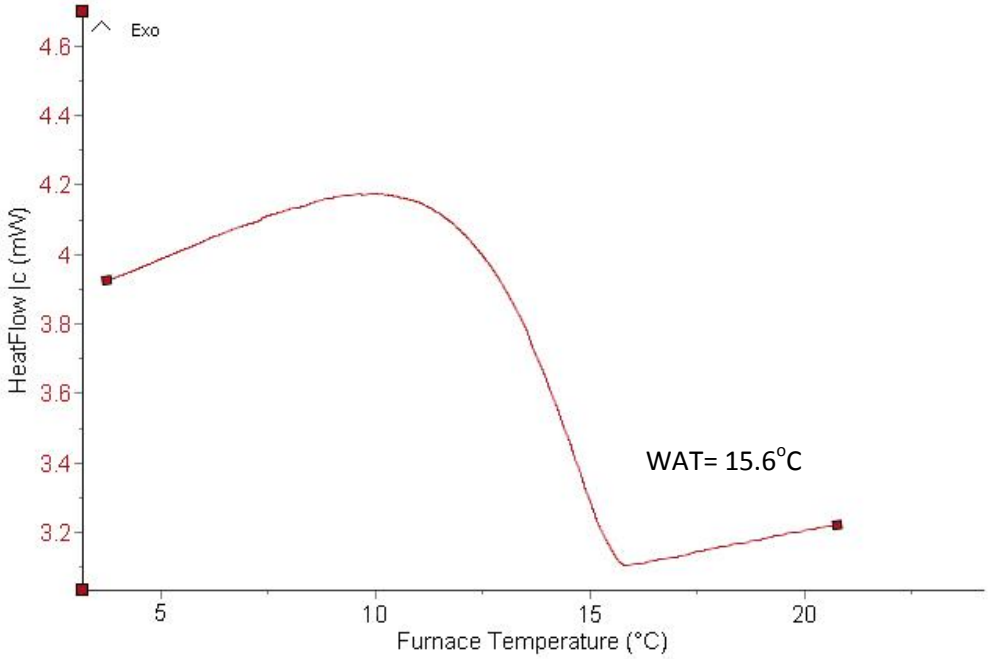

Figure 29: Graph of heat flow against furnace temperature for Dubai crude oil sample

The results for wax appearance temperature measured by using density meter are shown in figure 30, figure 31, figure 32 and figure 33. The wax appearance temperature can be determined by drawing a straight line over density data. A slight change of slope will indicate the wax appearance temperature of the sample. As observed, the curve for Dulang, Tapis, and Miri crude oil samples shows a clear and significant change of slope. However, for Dubai crude oil, there is no significant change of slope for the whole density data. This is due to the low content of wax in Dubai crude oil. Therefore, method of density meter is suitable only for crude oil samples with high wax content.

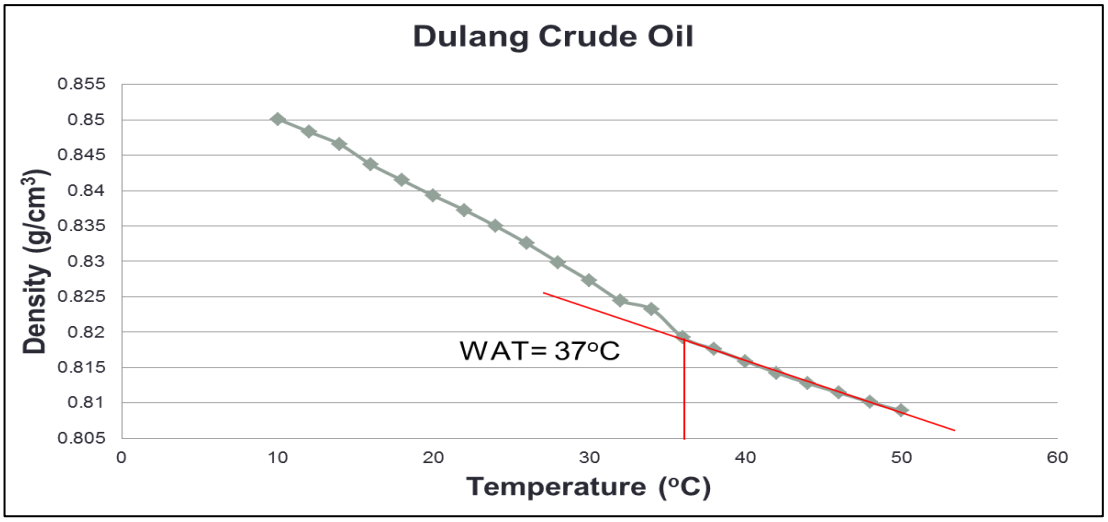

Figure 30: Graph of density against temperature for Dulang crude oil sample

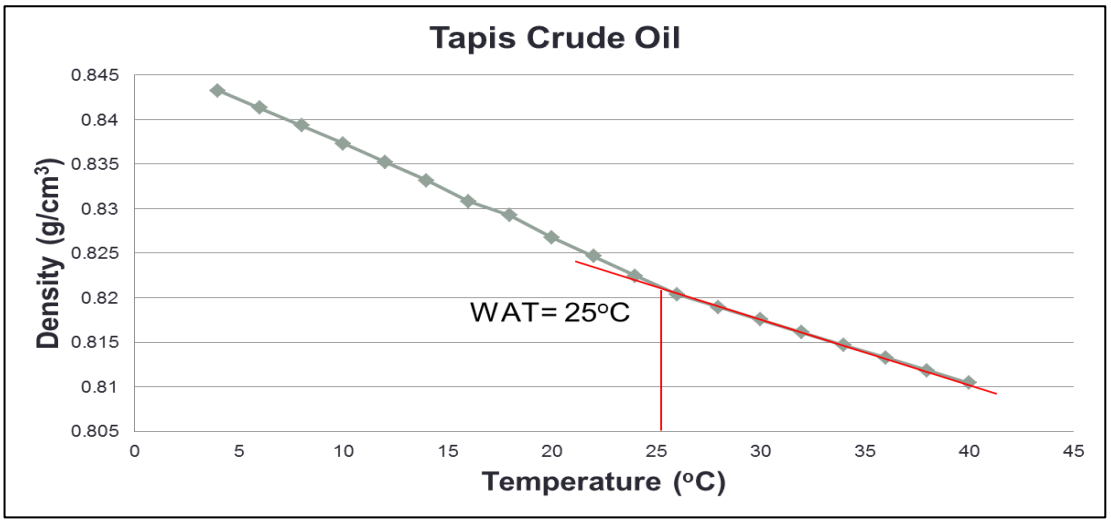

Figure 31: Graph of density against temperature for Tapis crude oil sample

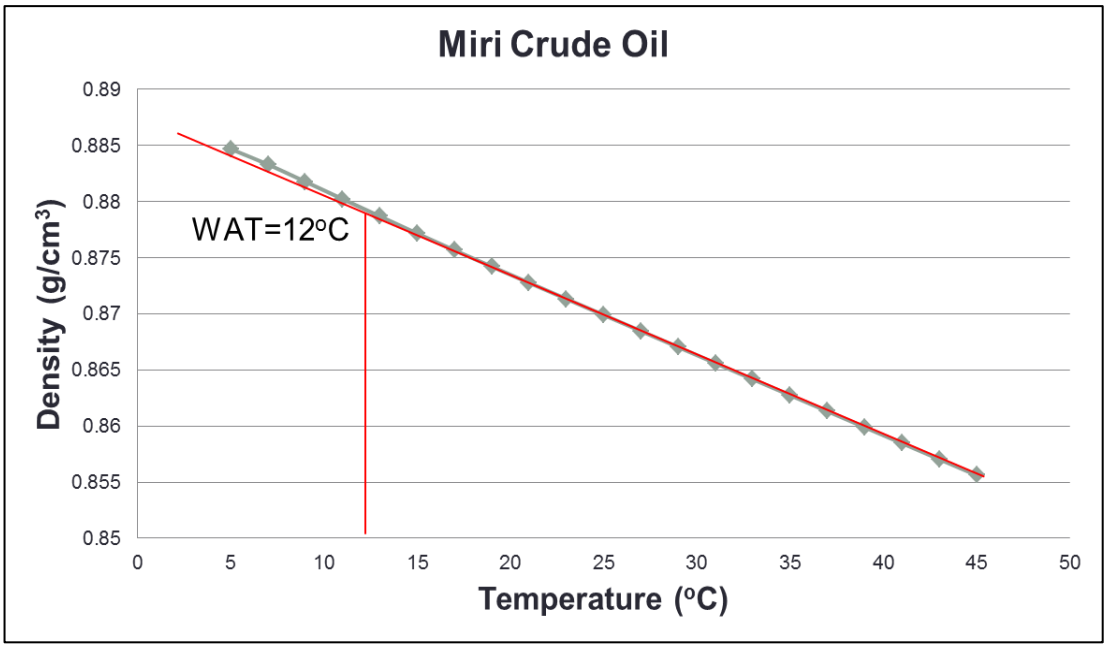

Figure 32: Graph of density against temperature for Miri crude oil sample

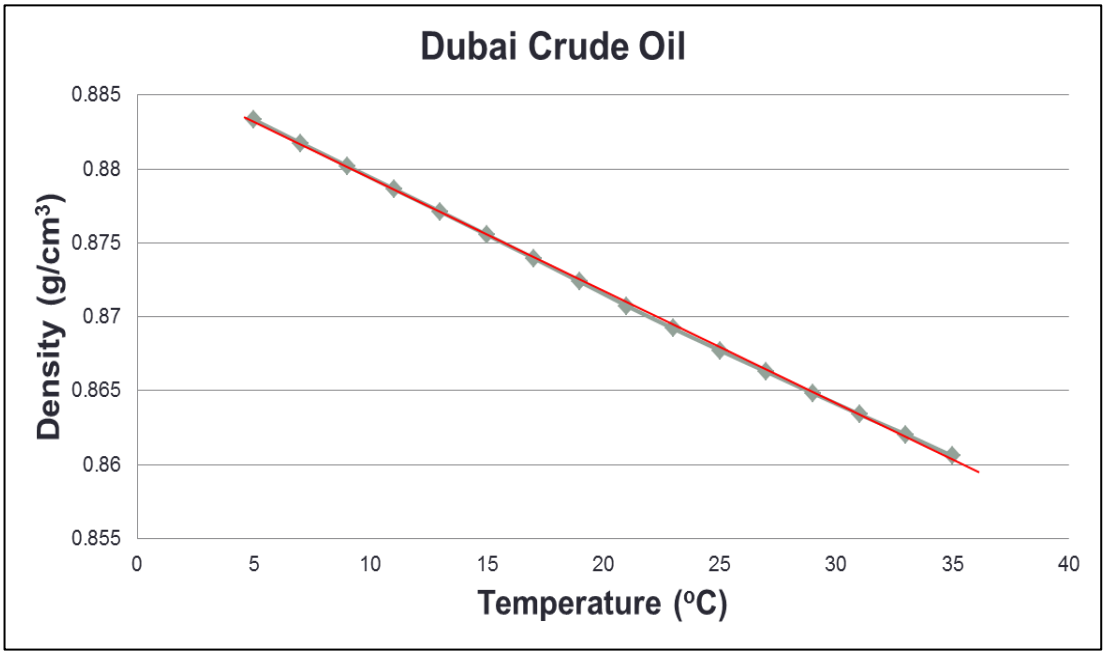

Figure 33: Graph of density against temperature for Dubai crude oil sample

Table 8 shows the wax content for each crude oil sample. Dulang crude oil has the highest total area percent followed by Tapis, Dubai and Miri.

Table 8: Wax Content

Sample	Wax Content (wt. %)
Dulang	28.5
Tapis	17.1
Miri	4.7
Dubai	6.2

By comparing the results obtained from Dulang, Tapis and Dubai crude oil samples, we can see a relationship between paraffinic composition, wax appearance temperature and wax content. Dulang crude oil with highest content of paraffinic composition seems to have higher wax appearance temperature and wax content while Dubai with lowest content of paraffinic composition seems to have lower wax appearance temperature and wax content. This relationship is important for development of wax deposition prediction models. Generally, heavier oil should have more wax than lighter oil strictly based on the definition of wax. Dulang, Tapis, Miri and Dubai were sorted by API gravity to compare wax content with increasing specific gravity. It is noted that the API gravity of the samples had no absolute relationship with the wax content.

As for SARA analysis, the presence and abundance of asphaltenes and high carbon number paraffins typically, but not always, indicates the potential for asphaltene and/or paraffin deposition during oil recovery. The relative abundance of aromatics and resins reduce the tendency of paraffins and asphaltenes to drop out of solution during petroleum production. Hence, the entire petroleum composition must be taken into account not only the presence of asphaltenes and paraffins, but also the relative abundance of aromatics and resins. If there are no asphaltenes and high carbon number paraffins present in a crude oil, no asphaltene and/or paraffin deposition should be expected. Their presence, however, does not necessarily imply problematic organic deposition.

4.5 Effect of CO_2 Injection on Wax Appearance Temperature

An experiment was conducted to study the effect CO_2 injection on wax appearance temperature. Dulang crude oil was run through continuous CO_2 flooding at 98^oC and 3000psia. The sample then was run through differential scanning to measure the wax appearance temperature. The result shows that the wax appearance temperature for Dulang crude oil after CO_2 injection to be 32.4^oC which is lower than the Dulang crude oil before CO_2 injection which is 37.2^oC. This is due to the effect of supercritical carbon dioxide which will dissolve the wax (Stauffer *et al*., 2000). Supercritical carbon dioxide occurred when the carbon dioxide was held above its critical temperature and critical pressure which is 30^oC and 1070psia respectively. Figure 34 shows the graph of heat flow against furnace temperature for Dulang crude oil after CO_2 injection.

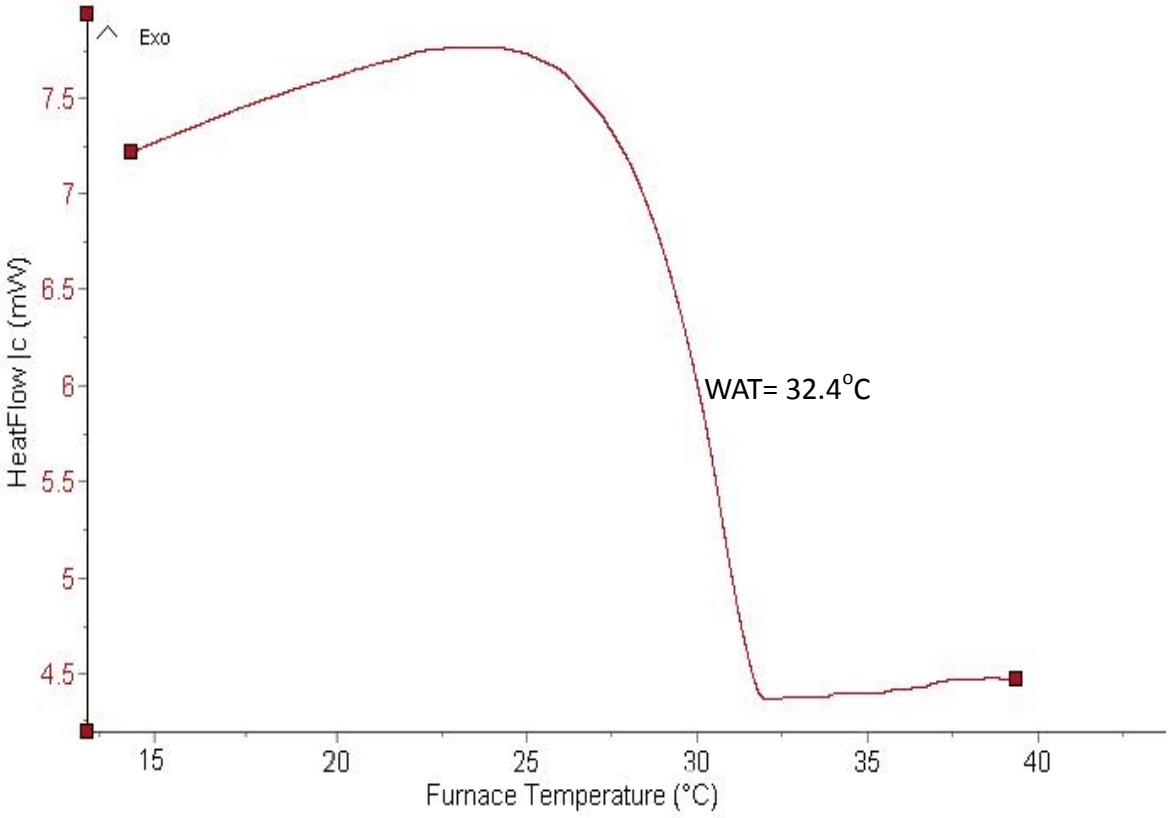

Figure 34: WAT of Dulang crude oil after CO_2 injection

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

The project which derived from a problem statement in which to study the problems related with the solid precipitation in the production system has successfully done. The key is to study the solid precipitation by using colloidal instability index and WAT method. All the objectives listed for this project have been achieved by using the experimental result from the laboratory by using various equipment and methods such SARA analysis, DSC, density meter, GCMS as well as UOP 46 method. However, with several available wax appearance temperature measurement techniques still have not been able to measure the true wax appearance temperature because each technique require some amount of wax to form for a detectable signal, the sensitivity and mode of detection varies for all techniques (Kulkarni *et al*. 2008)

Wax appearance temperature methods used in this work showed to be sensitive to the amount of wax content. DSC and density meter gave almost similar results of WAT for samples with high wax content. Result shows that crude oil with higher content of paraffinic composition will give higher wax appearance temperature as well as wax content. Dulang crude oil is identified to has the highest risk for both asphaltene and wax precipitation. A continuous CO_2 injection also is proved to affect the WAT as the result shows a decrease in WAT for Dulang crude oil. Besides, SARA fractionation was successfully quantified using available laboratory equipments which based on ASTM D 3279-97 and modified ASTM D 6591-06.

In order to improve the project execution and experimental result, there are several recommendations that need to be considered which are:

1) Early preparation need to be done to ensure the materials and equipment are set up properly and ready for the experiment.

2) Repetition of measurement should be practice to gain more reliable and accurate result.
3) More samples should be tested to have more rigid statement and justification.
4) Utilized more approaches to get the data of WAT such as Cross Polar Microscopy (CPM), Solid Detection System (SDS) as well as Fourier Transform Infrared Spectroscopy (FTIR).
5) Design the wax and asphaltene inhibitors (e.g. ionic liquid) and test it with flow loop.
6) Test the risk of solid deposition with different blending options. E.g. Dulang and Tapis.
7) Measure the wax curve for Malaysian crudes to justify with thermodynamic model.
8) Collaboration with oil and gas production companies, such as PETRONAS Research Sdn. Bhd is important to get more accurate result by using high quality samples as well as utilizing equipment with higher sensitivity.
9) Determine the mole percent of each carbon numbers as well as the molecular weight experimentally so that we can use it to predict WAT using empirical models.

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APPENDICES

Table 9: Gas chromatography data for Dulang crude oil

Carbon Number	Retention Time	Area Percent
C_8	4.156	0.112
C_9	6.945	0.230
C_{10}	9.678	0.310
C_{11}	12.562	0.214
C_{12}	15.512	0.940
C_{13}	18.340	2.368
C_{14}	21.025	2.172
C_{15}	23.549	3.089
C_{16}	25.937	2.670
C_{17}	28.226	4.204
C_{18}	30.364	2.961
C_{19}	32.419	2.437
C_{20}	34.379	2.296
C_{21}	36.254	2.079
C_{22}	38.048	1.999
C_{23}	39.770	1.927
C_{24}	41.421	1.899
C_{25}	43.014	1.959
C_{26}	44.542	1.828
C_{27}	46.020	1.732
C_{28}	47.442	1.565
C_{29}	48.818	1.320
C_{30}	50.141	1.343
C_{31}	51.429	1.167
C_{32}	52.668	0.662
C_{33}	53.880	0.574
C_{34}	55.045	0.310
C_{35}	56.185	0.225
C_{36}	57.299	0.130
C_{37}	57.617	0.561
C_{38}	58.504	0.254
C_{39}	59.876	0.215
C_{40}	61.460	0.554

Table 10: Gas chromatography data for Tapis crude oil

Carbon Number	Retention Time	Area Percent
C_8	4.192	1.752
C_9	6.405	2.276
C_{10}	9.151	2.534
C_{11}	12.082	2.120
C_{12}	14.979	2.222
C_{13}	17.770	2.844
C_{14}	20.426	3.014
C_{15}	22.919	3.292
C_{16}	25.283	2.927
C_{17}	27.546	4.584
C_{18}	29.658	2.740
C_{19}	31.702	2.398
C_{20}	33.639	2.382
C_{21}	35.486	2.391
C_{22}	37.261	2.241
C_{23}	38.962	2.358
C_{24}	40.596	2.175
C_{25}	42.163	2.136
C_{26}	43.668	1.930
C_{27}	45.128	1.906
C_{28}	16.520	1.639
C_{29}	47.874	1.530
C_{30}	49.165	1.036
C_{31}	50.429	0.906
C_{32}	5.636	0.520
C_{33}	52.826	0.439
C_{34}	53.966	0.200
C_{35}	55.084	0.150
C_{36}	56.168	0.135
C_{37}	57.223	0.111
C_{38}	58.504	0.036
C_{39}	59.666	0.020
C_{40}	61.143	0.050

Table 11: Gas chromatography data for Dubai crude oil

Carbon Number	Retention Time	Area Percent
C_8	4.170	2.215
C_9	6.365	2.261
C_{10}	9.089	2.187
C_{11}	12.003	2.265
C_{12}	14.895	2.279
C_{13}	17.675	2.066
C_{14}	20.308	2.400
C_{15}	22.807	2.120
C_{16}	25.166	1.709
C_{17}	27.417	1.992
C_{18}	29.652	0.953
C_{19}	31.573	1.318
C_{20}	33.510	1.153
C_{21}	35.363	1.238
C_{22}	37.132	1.033
C_{23}	38.962	0.094
C_{24}	40.456	0.801
C_{25}	42.084	0.618
C_{26}	43.528	0.669
C_{27}	44.976	0.500
C_{28}	46.380	0.434
C_{29}	47.823	0.345
C_{30}	49.148	0.292
C_{31}	50.305	0.266
C_{32}	51.529	0.219
C_{33}	52.793	0.189
C_{34}	53.871	0.153
C_{35}	55.106	0.120
C_{36}	56.140	0.124
C_{37}	57.392	0.098
C_{38}	58.554	0.090
C_{39}	59.857	0.063
C_{40}	61.351	0.015

Table 12: Gas chromatography data for Arab crude oil

Carbon Number	Retention Time	Area Percent
C_8	4.176	5.16
C_9	6.371	2.43
C_{10}	9.100	2.73
C_{11}	12.020	1.88
C_{12}	14.912	1.75
C_{13}	17.686	2.10
C_{14}	20.325	2.12
C_{15}	22.819	1.43
C_{16}	25.183	1.62
C_{17}	27.429	1.62
C_{18}	29.557	1.44
C_{19}	31.663	1.37
C_{20}	33.521	1.30
C_{21}	35.369	1.02
C_{22}	37.138	0.97
C_{23}	38.918	0.81
C_{24}	40.535	0.84
C_{25}	42.096	0.75
C_{26}	43.533	0.56
C_{27}	44.982	0.68
C_{28}	46.392	0.69
C_{29}	47.739	0.60
C_{30}	49.053	0.73
C_{31}	50.311	0.57
C_{32}	51.541	1.54
C_{33}	52.726	0.55
C_{34}	53.961	1.62
C_{35}	55.129	2.91
C_{36}	56.353	2.91
C_{37}	57.403	8.44
C_{38}	58.566	8.44
C_{39}	59.638	0.48
C_{40}	61.295	1.46

Table 13: Normal heptane insoluble measuring procedure

	A		B		
Sample	**Sample weight (gram)**	**Weight of crucible + glass fibre (gram)**	**Weight of crucible + glass fibre + asphaltenes (gram)**	**Insoluble weight (gram)**	**NHI % [(B/A) x 100]**
Dulang #1	1.0000	25.8805	25.8805	0.0000	0.000
Dulang #2	1.0076	25.8736	25.8754	0.0018	0.179
Tapis #1	1.0000	25.8695	25.8706	0.0011	0.110
Tapis #2	1.0027	25.8710	25.8726	0.0016	0.160
Miri Light #1	1.0046	25.8779	25.8792	0.0013	0.129
Miri Light #2	1.0000	25.8754	25.8766	0.0012	0.120
Dubai #1	0.9984	25.8397	25.8458	0.0037	0.371
Dubai #2	1.0034	25.8421	25.8452	0.0031	0.310
Arab #1	1.0002	25.8769	25.9072	0.0303	3.025
Arab #2	1.0056	25.8771	25.9137	0.0366	3.641

NHI = Normal Heptane Insoluble (Asphaltene)

Table 14: Measurement of saturates and aromatics percentage for crude oils

Sample	Sample weight (g)	Asphaltene (g)	Asphaltene (wt%)	Maltene (g)	Maltene (mg)	Sample injection (ml)	Maltene injected (mg)	Resin (mg)	Resin (wt%)	Saturates & aomatics (wt%)
Dulang	1.0076	0.0018	0.18	1.00580	1005.80	6.300	48.74	1.10	2.256752108	97.56
Tapis	1.0014	0.00135	0.13	1.00000	1000.00	10.20	78.46	1.37	1.746078431	98.12
Miri	1.0023	0.00125	0.12	1.00105	1001.05	10.15	78.16	26.9	34.41706405	65.46
Dubai	1.0009	0.0034	0.34	0.99750	997.500	10.20	78.27	16.3	20.82657624	78.83

Table 15: Concentration of calibration components

Calibration Standard	Cyclohexane (g/100mL)	O-Xylene (g/100mL)	Cyclohexane + O-Xylene (g/100mL)	Area of cyclohexane	Area of O-Xylene	Saturates (%)	Aromatics (%)
A	5	4	9	700231.9	1665691.9	55.56	44.44
B	2	1	3	281287.3	415751.6	66.67	33.33
C	0.5	0.25	0.75	71595.6	105265.3	66.67	33.33
D	0.1	0.05	0.15	17520.9	21086.7	66.67	33.33

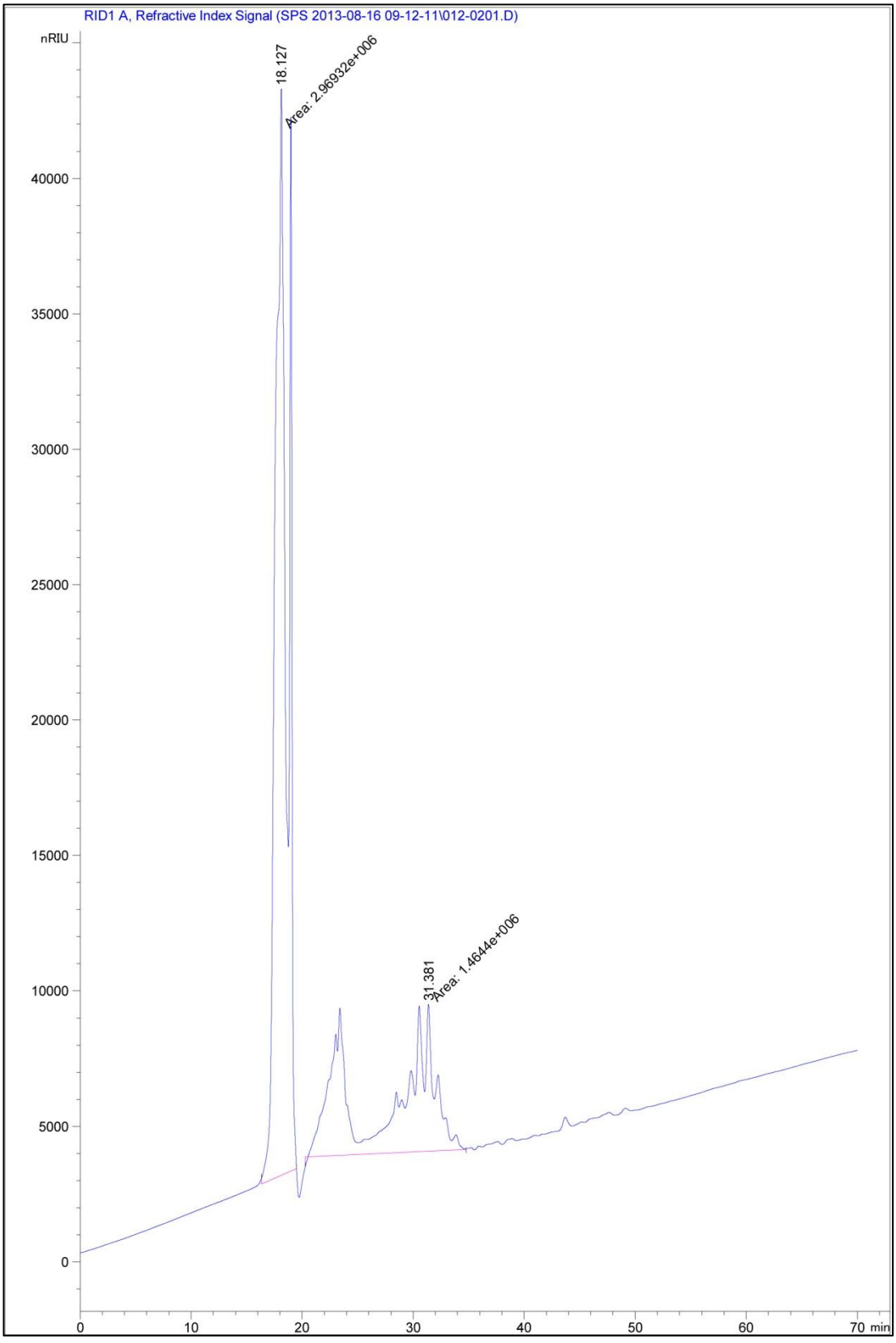

Figure 35: Refractive index signal for Dulang crude oil

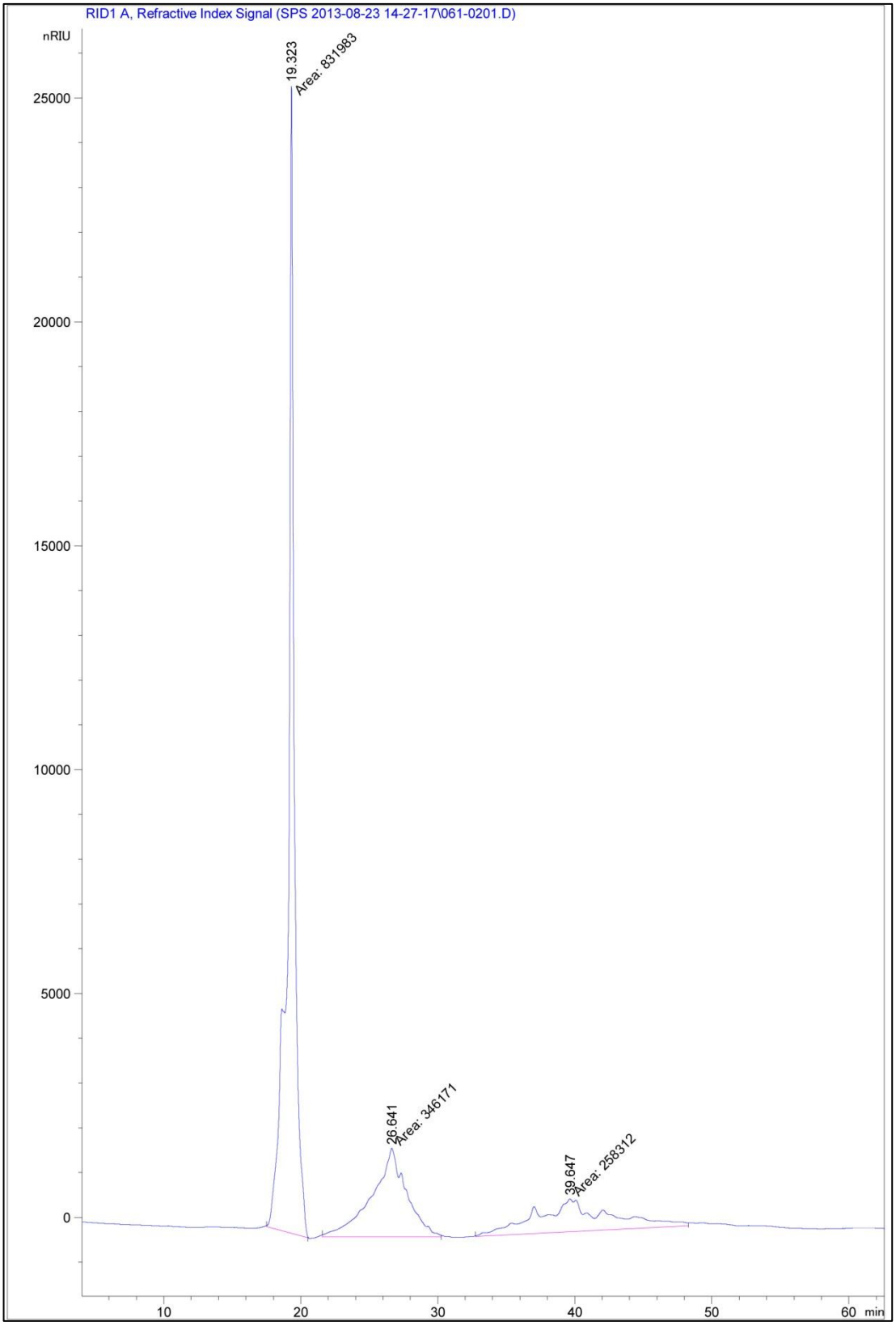

Figure 36: Refractive index signal for Arab crude oil

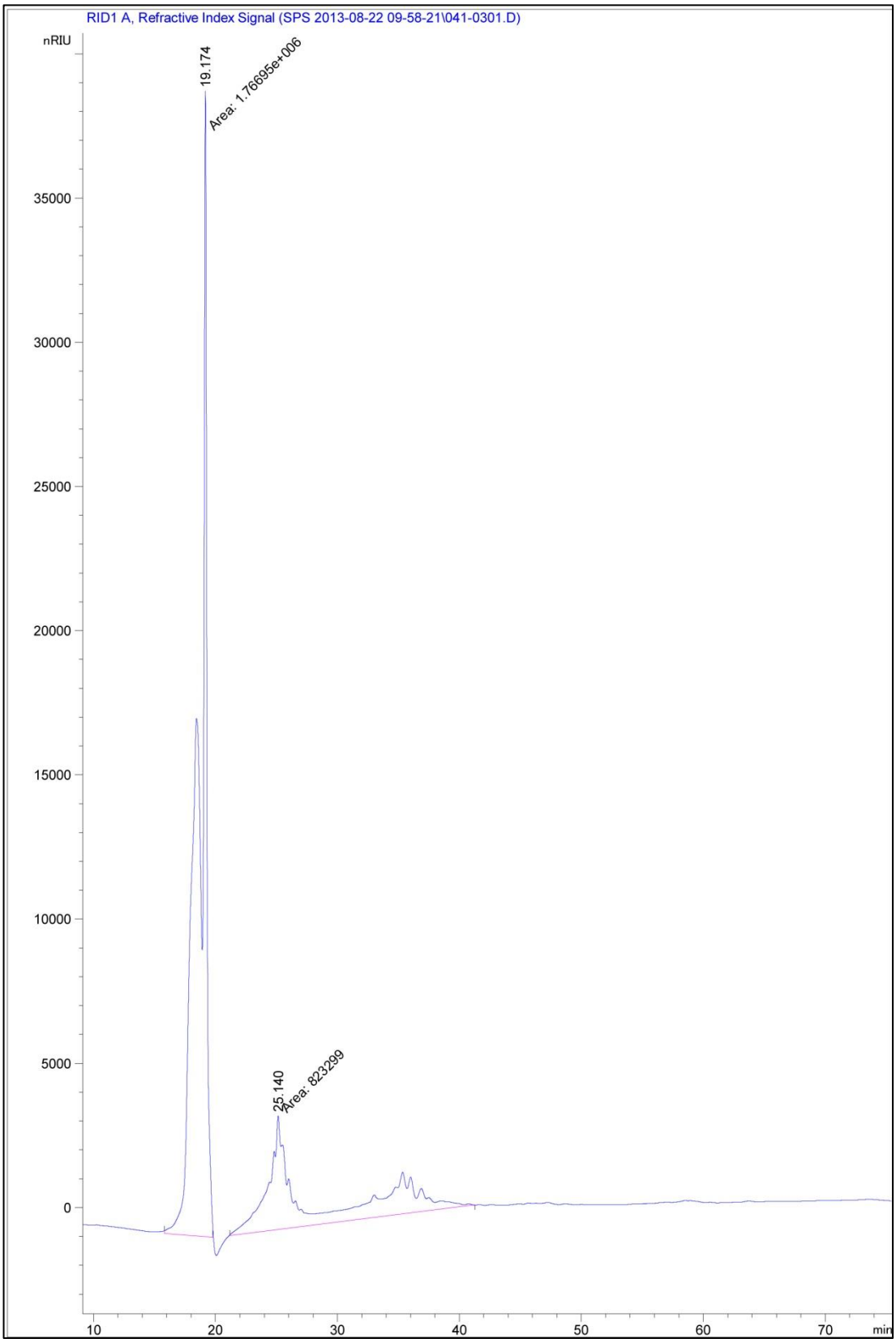

Figure 37: Refractive index signal for Tapis crude oil

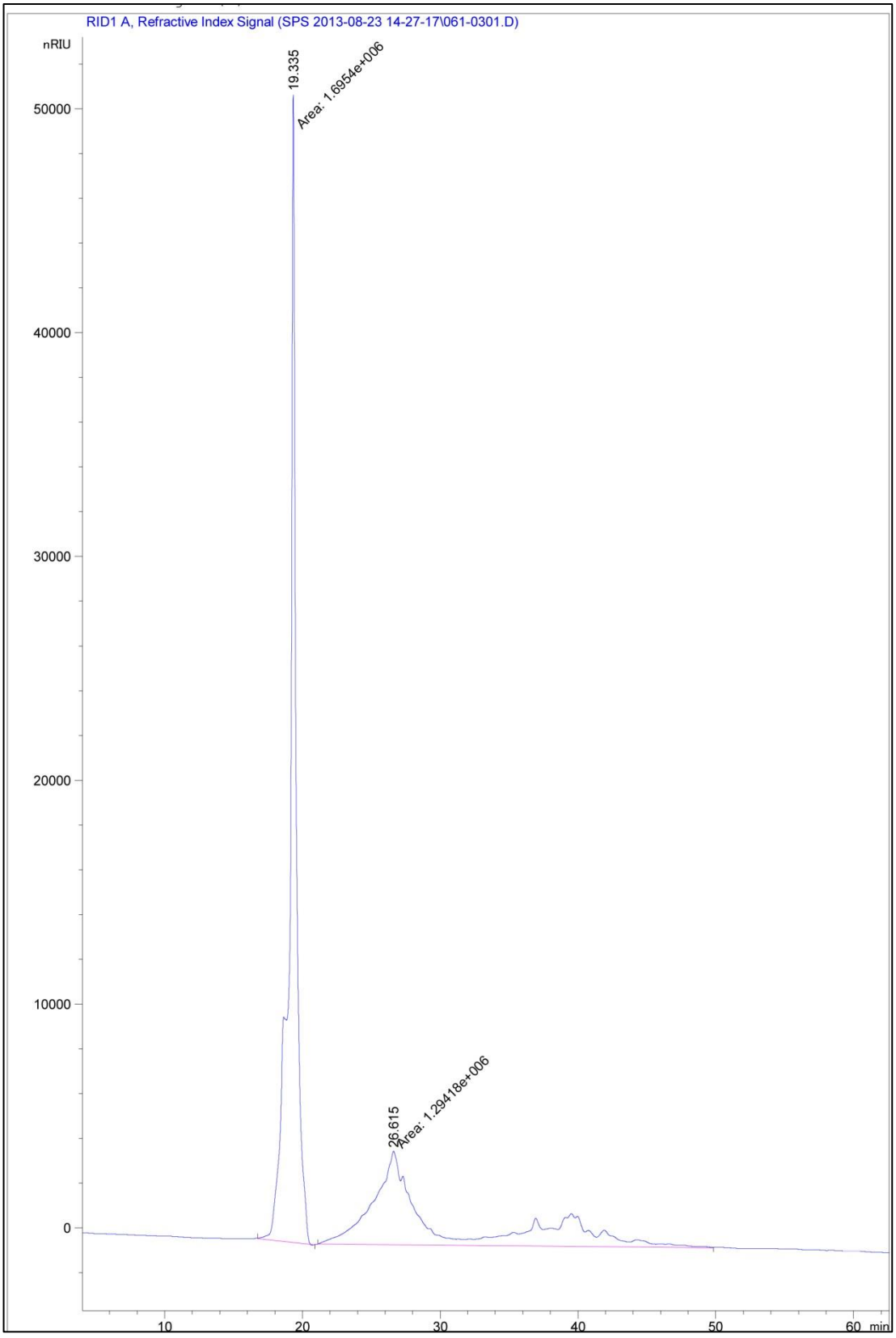

Figure 38: Refractive index signal for Miri crude oil

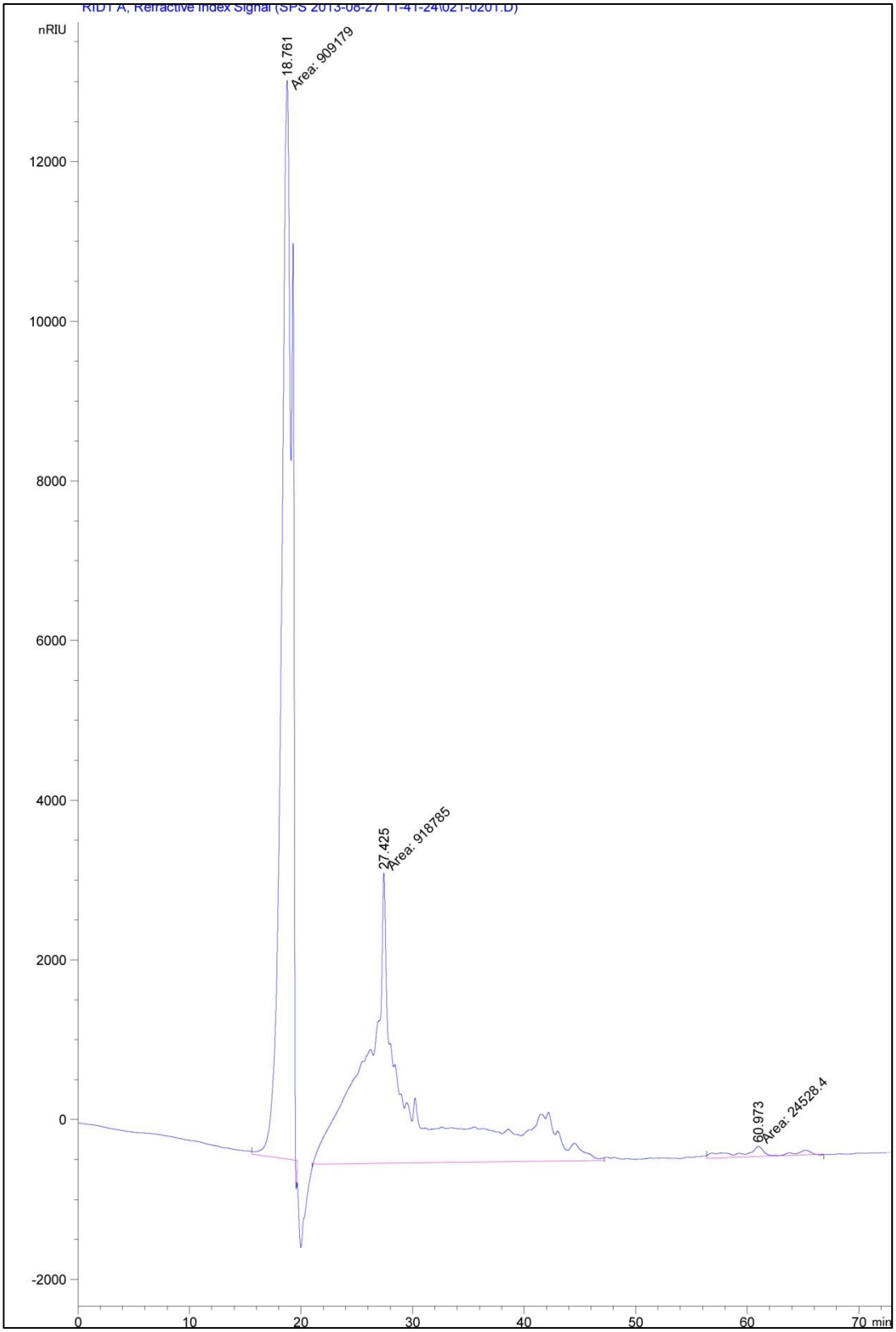

Figure 39: Refractive index signal for Dubai crude oil