A Study on Asphaltenes Precipitation in Crude Oil Using Different Titrant

by

Nur Aida Binti Nur Hardy

15253

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
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Universiti Teknologi PETRONAS
32610, Bandar Seri Iskandar
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

____

(AP. Dr. Marappagounder Ramasamy)

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK

September 2015

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 references and acknowledgement, and that the original work contained herein have not been undertaken or done by unspecified source or persons.

NUR AIDA BINTI NUR HARDY

ABSTRACT

Asphaltenes are defined generally in terms of solubility. Its molecular structure in crude oil is said to be indefinite, making it difficult to study on the asphaltenes precipitation, which has been the problems to oil and gas industry for long period of time. Although different studies have been done to understand the precipitation and deposition of asphaltenes, the concrete conclusions are rare and still debatable. Examining through the past studies, the effects of oil composition and titrant type are analyzed to be able to explain further on the subject. SARA composition analysis is applied to represent oil composition where there are saturates, aromatics, resins and asphaltenes. Based on a study on the effect of bulk temperature on asphaltenes precipitation, Automated Flocculation Titrimeter which is referring to Heithaus test method becomes the major equipment and concept to be used to conduct the study in this project. The results from the test method requires determination on the Hildebrand's solubility parameters which correlates with the relation between asphaltenes solubility and precipitation; high asphaltenes solubility, low possibility of precipitation. However in this report, the applicability of Heithaus Parameters are the only method of analysis discussed.

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I am also greatly thankful to Mr. Muhammad Azhar Mohamad Yusop, a research officer in Crude Oil Fouling Research lab, who has been ensuring my safety and convenience in conducting lab work in the laboratory. He has helped me in acquiring some chemicals and equipment.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background

Asphaltenes are defined as insoluble in paraffinic solvents and soluble in aromatic solvents. They are considered to have high molecular mass and high carbon-hydrogen ratio (Nikooyeh, 2012, p. 24). In terms of the molecular structure, they are yet to come to a unanimous explanation. Asphaltenes behavior in crude oil such as their phase transition and stabilization mechanism are very much like the structure, are still debatable that lead to difficulties in concrete understanding of this petroleum component.

The studies on asphaltenes have become very important to understand factors that lead to asphaltene precipitation and deposition. These phenomena of asphaltenes in upstream and downstream processes in oil and gas industry have clogged wells, blocked pore spaces that leads to fouling of equipment and more problems that would lead to inefficient processes and loss of profit. In refinery process, fouling can happen at any stage during production, dewatering, desalting, distillation and many more (Speight, 2015, p. 205). Especially in downstream process, the issue of fouling has become wide due to the usage of more heavy oil that is said contribute to more resins and asphaltenes fraction. These resins and asphaltenes constituents can cause problems through coke formation and phase change of insoluble products. It is also believed that the formation of solid components happen due to changes of pressure, temperature, and composition especially in the production field. (Akbarzadeh, 2007, p. 23). At any situation, this precipitation has caused costs to oil and gas industry.

There are a few methods that have been developed for understanding the asphaltenes precipitation. Along with the procedures, analyzing results are also critical to interpret any results obtained numerically and later reflect to the theories. Anderson (1999) applied the flocculation onset titration method to estimate asphaltenes precipitation and stability in crude oil. Hildebrand's solubility parameters are the widely used numerical interpretation of flocculation experimental results. This mathematical modelling has been used in predicting asphaltenes precipitation and solubility for different crude oils at different operating conditions. Recently, a study of temperature effects using Automated Flocculation Titrimeter (Zubair, 2014) has been reported in literature. The findings from the study and recommendation given were taken into consideration for further studies.

1.2 Flocculation/Precipitation

In the study of asphaltenes precipitation, the mechanism of how asphaltenes are being flocculated and precipitated are mentioned in numerous studies. A study have shown that asphaltenes precipitation is not reversible (Peramanu, Clarke, & Pruden, 1999). This indicates that asphaltenes are not in completely dissolved state in oil where it can be partially in colloidal state. In dissolved state, asphaltenes are not surrounded by other molecules while in colloidal state, they are surrounded by resins molecules. Another study has also mentioned both precipitation is reversible and not reversible. In reversible case, asphaltenes exist in true liquid state. Precipitation depends on thermodynamic properties such as temperature, pressure and composition (Sheu, Mullins, & Fine Particle Society, 1995, p. 193).

1.3 Problem Statement

The existing studies on asphaltenes precipitation are inconclusive in their conclusions on the mechanism of asphaltenes precipitation. Different views and contradicting results give huge impact to the overall understanding of the topics. These may be caused by different factors; temperature, pressure and etc. Different composition and concentration of asphaltenes and crude oil are believed to be contributing. Not only the asphaltenes composition, had studies also stated the effect of other oil composition such as saturates. This indicates the indefinite relation between oil composition and the precipitation. Additionally, the type of titrant are yet to be widely discussed but the different types should give different precipitation behavior. Hence, more studies on both parameters should be further researched and tested to produce a better explanation.

1.4 Research Objectives

Based on the background studies and problems defined, two parameters are believed to be contributing in the asphaltenes precipitation studies. Below are the defined aims.

- To study on the effect of oil composition to asphaltenes precipitation
- To study on the effect of titrant type to asphaltenes precipitation

The study on the oil composition is done by changing the type of crude oil used, in line with the different titrant used. Other parameters that may affect the study are strictly fixed. Several stages of result analysis are to be applied in order to reach the overall conclusion.

1.5 Scope of Study

Based on the defined objectives, the study on the two parameters are confined and defined to characterize the oil composition and titrant type. The concept in the study is focused on titration mechanism under automated condition. The UV light transmittance passing through the titrated crude oil will interpret on the time taken for asphaltenes to start precipitate which is called the flocculation onset point. This value will be used for further analysis.

1.5.1 Oil composition

The composition of crude oil is initially represented by asphaltenes composition gained from crude assay. It is used to define the significance of understanding the relationship between saturates, aromatics, resins, and asphaltenes that mainly contribute to the composition. In the later stage, SARA composition is to be measured to discover on how each composition can be affecting the precipitation under the method used.

1.5.2 Titrant type

Different types of n-alkanes are used as titrant to promote precipitation of asphaltenes. It is used especially to study on asphaltenes precipitation in industrial world. The measuring factor for the n-alkanes are the carbon number. The relationship between the carbon number of commonly used n-alkanes and the asphaltenes precipitation behavior are to be analyzed in the study.

CHAPTER 2

LITERATURE REVIEW

2.1 Automated Flocculation Titrimeter

In the study of asphaltenes precipitation, AFT is commonly used to determine the effects of several parameters to precipitation. Based on the studies by Zubair, et al., Heithaus test method and Hildebrand solubility parameter can be derived from the result of AFT data. From these, the solubility and stability of the system involved can be analyzed. Heithaus test method has be applied for more than 30 years ago on compatibility of asphaltenes system. Compatible asphaltenes mean materials are well peptized by maltenes due to strong associations or dispersed materials are in small amount. Incompatibility means materials are not well peptized by oil (Pauli, p. 1276). The Heithaus Titrimetry which is in accordance with ASTM D6073-01 calculates three parameters in order to predict the colloidal stability of oils. These parameters are: (i) A measure of overall colloidal stability of asphalt, *P*; (ii) Pa is to measure the peptizability of asphaltenes; (iii) Po is the value of solvating power of oil. Oil with P value lower than 2.5 is considered to be less stable and vice versa. High Pa value indicates the lower the colloidal stability of asphaltenes and vice versa in a system, where high values of Po indicate increasing solvency characteristic of dispersing phase (Zubair et al. 2015). Equations below show how the parameters are being calculated.

$$P = Po/(1 - Pa)$$

$$Pa = 1 - FRmax$$

$$Po = FRmax * ((\frac{1}{Cmin}) + 1)$$

$$FR = Vs/(Vs + Vt)$$

$$C = Wo/(Vs + Vt)$$

(1)

FR which stands for flocculation ratio is the fraction of volume of solvent to the total volume of solvent-titrant mixture at flocculation onset point. FRmax is determined by plotting the relevant FR values to get the intercept. C stands for dilute concentration of ratio of mass of oil to the volume of titrant and solvent at flocculation onset point. Similar with FRmax, Cmin is determined from the plot's intercept. According to the test method, higher Cmin represent lower stability of oil.

Hildebrand's Solubility Parameter reflects the numerical value relative solvency behavior of specific solvent (Burke, 1984). It is derived from cohesive energy density and helps to clarify on Van der Waals theory and solubility. It is stated that maximum solubility occurs when solute and solvent cohesive energy densities are closer.

2.2 Effect of oil composition

The composition of crude oil is usually categorized into four; saturates, asphaltenes, resins and aromatics. Within each class, the non-hydrocarbon, the organic molecules also contribute to its complexity. In lighter low-sulfur paraffin-base crude oil would have higher hydrocarbon content up to 97% compared to high-sulfur asphalt-base crude oil (Speight, 2015, p. 53). The more the aromatic is the oil, the larger the flocculation Metallic contents in crude oil can originally be found in the oil or being picked up during storing, handling and processing. The common metals are vanadium, nickel, sodium, iron, silica etc. It is said that the higher the content of metals, the higher the possibility for fouling to happen especially in refinery process (Speight, 2015, p. 24).

As mentioned in many studies, asphaltenes fraction becomes the major attention in fouling problem. As asphaltenes concentration increase, the number of individual particles also increase (Rastegari et al 2004). Flocculation rate also increases. This may be explained by increasing number of asphaltenes that precipitates indicating higher proportion of asphaltenes. The change in molecular structures of asphaltenes can lead to phase changes and formation of solid. The organic nitrogen consisted in the asphaltenes and resins constituents can become insoluble due to thermal reaction. Some of the bonds in the system can be affected and initiate thermal decomposition (Speight, 2015, p. 149).

A study by Chamkalani states that asphaltenes precipitation does not come from the high asphaltenes fractions but saturates. The SARA fractions are said to be contributing to asphaltenes stability. Stability of a colloid dispersion defines its resistance to flocculation. Another study also concluded the contribution of SARA fractions to asphaltenes flocculation over asphaltenes fraction alone. The relationship between dispersed particles and flocculated particles are measured in colloidal index (Peramanu, Clarke, & Pruden, 1999). Some simple calculations are stated by using SARA fractions to understand the stability of asphaltenes. This method is applicable to average medium opacity oil.

$$(RI)oil = 0.001452 + S + 0.0014982 * A + 0.0016624 * (R + As) \quad (2)$$

$$\Delta(RI) = (RI)oil * PRI \quad (3)$$

Where S is saturate, A is aromatic, R is resin and As is asphaltenes percent.

PRI = 1.44 (Assumption). When Δ(RI) > 0.06, it is more likely to have stable asphaltenes. Δ(RI) less than 0.045 is said to have asphaltenes deposit problems. While crude oil with $0.045 < \Delta(RI) < 0.06$ are in the border region. Another study proposes theory on Colloidal Stability Index, CII; CII <0.7 stable, CII>0.9 unstable. (Yen, Yin, & Asomaning, 2001, p.2)

$$CII = (saturates + asphaltenes) / (aromatics + resin) \tag{4}$$

2.3 Effect of titrant type

Injection of titrant to promote precipitation is said to have variation depending on the type of solvent. According to Arciniegas & Babadagli, as the carbon number of solvent decreases, the floc size increases. Comparing to propane and butane, n-heptane is more of solvent due to its less viscosity reduction hence is slower in precipitating asphaltenes and resins. The lower carbon number solvent would be reducing the solubility of asphaltenes. In their experimental work, they concluded that at room temperature, solvent n-decane has higher solubility parameter than n-hexane. Another study by Peramanu et, al. supports the concept of solvent with high carbon number has high solubility parameter. As the carbon number increases, the solubility parameter of solvent approaches resins'. This encourages the bond between resins and solvent to overcome the equilibrium adsorption between resins and asphaltenes.

2.4 Summary

Based on the literature reviews, the applicability of Automated Flocculation Titrimeter can be used even by changing the parameters. The different views on the effect of oil composition can be further investigated. The scope to represent oil composition can be represented by fractal composition of saturates, aromatics, resins and asphaltenes. The relationship between titrant and the precipitation behavior are ambiguous, which should be experimented by manipulating the different types of titrant.

CHAPTER 3

METHODOLOGY

3.1 Equipment

The major equipment to be used in this experimental work is Automated Flocculation Titrimeter. Several parameters are set and adjusted to determine their effects toward the Heithaus parameters and Hildebrand's solubility parameters. The effect of oil composition is further reinforced by determining SARA composition. High Performance Liquid Chromatography is used for measurement purpose. Figure 3.1 shows the front look of the equipment to be used. Figure 3.2 shows the diagram flow in the equipment. Figure 3.3 is the diagram of a HPLC that will be used as a measurement tool for crude oil composition. Table 3.1 summarize the functions of certain important parts of the equipment.

Figure 3. 1 Automated Flocculation Titrimeter

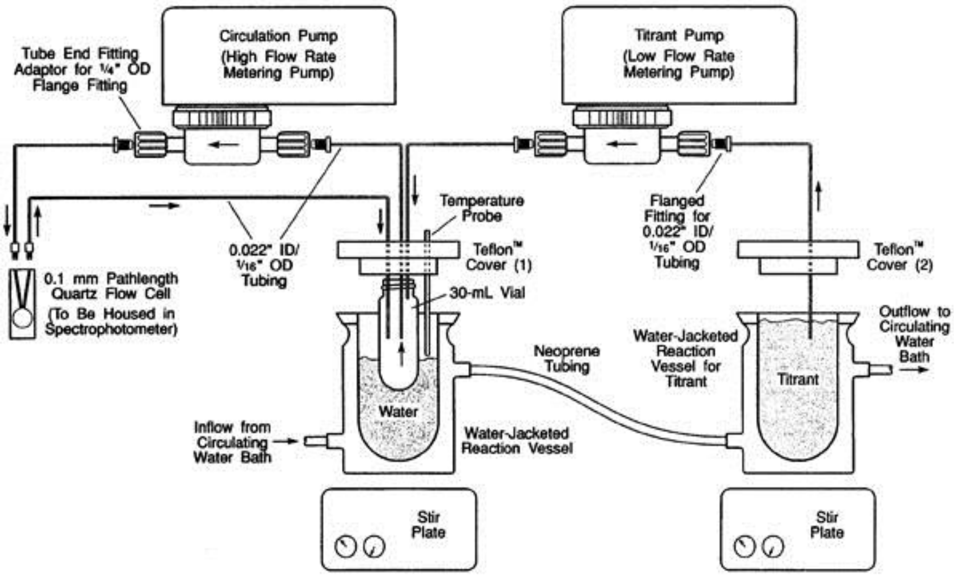

Figure 3. 2 Flow diagram of AFT

Figure 3. 3 High Performance Liquid Chromatography

Table 3. 1 Important parts of AFT

Parts of the AFT K47190	Functions
Water-jacketed reaction vessels	For continuous mixing of solution
Thermometer probe	To measure temperature (20-100°*C)*
Refrigerated water bath circulator	To provide chilled water
Metering pumps	For high & low flow rate
Visible spectrophotometer	To transmit light (380nm – 1050nm)
Data acquisition system	Propriety software AFT central
Flow loop & accessories	To make flow loop

3.2 Experimental Design

Based on the studies done earlier, the crude oil composition and the titrant type are to be manipulated in the experimental work. The controlled variables are also defined for further design. The table below shows the details of materials and variables to be applied.

Table 3. 2 Experimental Variables

<table>
<tr><th>Variables</th><th>Parameters</th><th>Description</th><th>Remarks</th></tr>
<tr><td rowspan="5">Manipulated Variables</td><td rowspan="3">Crude Oil</td><td>Wafra Ratawi (WR) – Medium</td><td rowspan="3">0.4, 0.6, 0.8g</td></tr>
<tr><td>Pyrenese (PY) - Heavy</td></tr>
<tr><td>Arab Light (AL) - Light</td></tr>
<tr><td rowspan="2">Titrant</td><td>Isooctane – a</td><td rowspan="2">0.3mL/min</td></tr>
<tr><td>Heptane - b</td></tr>
<tr><td rowspan="3">Controlled Variables</td><td>Temperature</td><td>60 degrees Celsius</td><td></td></tr>
<tr><td>Solvent</td><td>LC grade Toluene</td><td>3mL</td></tr>
<tr><td>Pressure</td><td>1 atm</td><td></td></tr>
</table>

Within first 7 weeks, the focus is on getting result by manipulating crude oil and solvent used. Each set of experiment is repeated at least three times to check the repeatability and accuracy. Average is calculated for other calculation purpose when necessary. Table 3.3 shows the overall experimental work strategy for 7 weeks period.

Table 3. 3 Experimental Matrix

Crude Oil	**WR**		**PY**		**AL**	
Solvent	**a**	**b**	**a**	**b**	**a**	**b**
Weight, W_o (g)	**1**		**2**		**3**	
0.4	1-a	1-b	2-a	2-b	3-a	3-b
0.6	1-a	1-b	2-a	2-b	3-a	3-b
0.8	1-a	1-b	2-a	2-b	3-a	3-b

3.3 Crude Oil & Titrant Properties

The crude oil properties are used as reference for analysis purpose. Three types of crude oil are chosen to be investigated on and represent three different crude type. Primarily, the asphaltenes content is the benchmark in analyzing the effect of oil composition towards asphaltenes precipitation. Later, the SARA content help to clarify on the effect of oil composition. The properties are defined in table 3.4 below.

Table 3. 4 Crude Assay of Crude Oil

Properties	**Crude Oil**		
	WR	PY	AL
Origin	Neutral Zone	Australia	Saudi Arabia
Crude Type	Medium	Heavy	Light
Chemical Class	Naphthenic	Intermediate	
API Gravity @ 60 F	24	18.7	32.8
Density @ 15 deg C (kg/l)	0.9069	0.9415	0.858
Asphaltenes (%)	5.4	0.2	1.6
Carbon Content (%)			87.8
Hydrogen Content (%)			12.1
Carbon Residue (%)			1.58
Mercury (ppb)	1	1	
Iron (ppm)	2.6	6	0.8
Vanadium (ppm)	47.553	<1	21.172
Nickel (ppm)	22.285	2	7.982

The properties of titrant used are also summarized in the table below. Other than the carbon number, other properties are important in analyzing the effect of different types of titrant.

3.4 Experimental Procedures

The detailed steps in conducting the experimental work are described below.

3.4.1 Preparation of Sample

i. 3 samples are prepared for each weight, W_o (0.4g, 0.6g. 0.8g)
ii. Crude oil samples in a 30mL vial are weighed accordingly using weighing electronic balance machine by Shimadzu (AX120)
iii. Samples are diluted with 3mL of Liquid Chromatography Grade Toluene, V_s. Vials walls are ensured to be clean and free from crude oil spots
iv. Samples are left for 12 hours under fume hood

3.4.2 Preparation of AFT (Automated Flocculation Titration)

i. Power plugs, temperature controller power, AFT power are switched on
ii. Temperature setting is set 60 degrees Celsius
iii. Water is inserted into both water-jacketed reaction vessel that surround titrant and samples vials for heat transfer
iv. Toluene is prepared beside the sample vial (for cleaning purpose throughout the experiment)
v. Titrant vial is filled with titrant (LC grade iso-octane, C5, C6, C7)
vi. AFT Central is started once the computer is switched on
vii. 'Power Strip' is checked
viii. Test Run is started with toluene being circulated as sample for cleaning and checking purpose
ix. The transmittance will be at 100% and automatically calibrated

3.4.3 Test run with AFT

i. Sample vial is placed in the sample vessel and closed with Teflon cover
ii. The inlet and outlet tubing (is placed into the sample vial
iii. The outlet titrant tube is placed into the sample vial as well
iv. ‘Test Run’ is clicked from the AFT Central
v. The ‘Sample ID’, ‘Mass, W_o ’, ‘Titrant flow, V_t’, ‘Solvent volume, V_s’ are entered. V_t = 0.277ml/min, V_s = 3mL
vi. The test is started. The pumps are also started automatically
vii. The light transmittance pattern is observed commonly for 30 minutes
viii. The flow of sample through the pump and the flow of titrant are ensured to be normal throughout the test
ix. When the test run is stopped, the results are saved
x. The inlet and outlet tubing of sample are to be cleaned by allowing Toluene to circulate through for several minutes
xi. The sample vial is taken and the sample is thrown away as wastes
xii. Results are exported to excel sheet
xiii. Test run is repeated when the outlet and inlet tubing of sample are cleaned and emptied from old sample.

3.4.4 Cleaning

i. Sample vials are rinsed with LC grade Toluene before being washed with water and soap
ii. Sample vials are kept in oven at for 12 hours at maximum 60 degrees Celsius before being used again to ensure water and toluene are evaporated

3.5 SARA Analysis

SARA analysis is done to analyze the impact between saturates, aromatics, resins and asphaltenes as oil composition to the precipitation. The three different crude oils are to be measured using High Performance Liquid Chromatography and weight manual calculation. Asphaltenes are to be separated from maltenes before measurement can be done.

3.5.1 Asphaltenes separation

i. Hot plate and reflux condenser are set up.
ii. Crude oil is weighed using scale at 1g and inserted into glass flask
iii. 100mL of n-heptane is poured into the glass flask. Stirrer is inserted before flask is closed
iv. A weighing vessel with filter paper are kept in oven at more than 100 degrees Celsius for 15 minutes. It is weighed after the vessel is cooled off for 15 minutes. The weight of vessel at this stage is W_o.
v. Glass flask containing crude oil is placed in a hot tub on hot plate.
vi. Flask is connected to condenser and water is set to flow.
vii. Crude oil is heated up to boiling point of around 97 degrees Celsius and let it boil for 30 minutes.
viii. After 30 minutes, glass flask is set to cool down until 50 degrees Celsius.
ix. A filtration flask is set to connect with pump
x. Cooled down crude oil is poured into the weighing vessel with filter paper positioned on the filtration flask.
xi. 10mL, 5mL and 5 mL of N-heptane are added to crude oil to allow asphaltenes to flocculate.
xii. The weighing vessel is then placed into oven for 15 minutes at more than 100 degrees Celsius.
xiii. The weighing vessel is then weighed after it is cooled off for 15 minutes to get the weight of asphaltenes collected, W_f.
xiv. The amount of asphaltenes are calculated as below.

$$\%asphaltenes = \frac{Wf - Wo}{Wo} \tag{5}$$

3.5.2 Maltenes Analysis

Standards are prepared to produce calibration curve to measure other composition includes saturates and aromatics. Saturates and aromatics are represented by cyclohexane and xylene respectively in High Performance Liquid Chromatography.

i. Standards of different cyclohexane and xylene composition are prepared in vials: A, B, C, D.
ii. Standards are injected into columns and the area under the curve for refractive index are calculated for calibration curve plot.
iii. Dichloromethane is injected to flush resin out.
iv. Resin solution is inserted into a glass flask to allow evaporation to occur using rotary evaporator.
v. The residues formed in the glass are taken as the resins.
vi. The amount of resins are calculated as below

$$\frac{weight\ of\ crude\ oil(exclude\ resins\ \&\ asphaltenes)}{weight\ of\ resins} = \frac{\%crude\ oil}{\%resins} \quad (6)$$

3.6 Result Analysis Method

As mentioned in literature review, several analysis methods are essential in applying the theories to the real practical work. There are in overall 4 methods to analyze data from AFT experiment; Heithaus parameters, Hildebrand's solubility parameters, colloidal stability index and refractive index. Both Heithaus and Hildebrand's parameters are calculated based on the raw data from AFT result. CII and RI are calculated as additional method based on SARA composition. Both CII and RI are considered to support and help to explain the logicality of the main parameters.

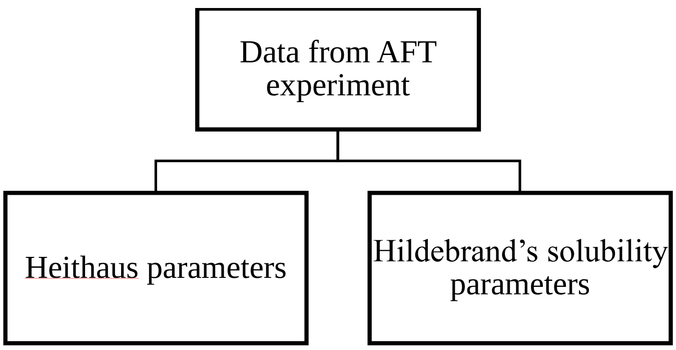

Figure 3. 4 Figure Analysis Method

3.7 Gantt Chart & Milestones

Tasks/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Experimental Work															
Progress Report Preparation								A							
Pre-Sedex Preparation											B				
Draft Final Report Preparation											C				
Dissertation (Softbound)Preparation												D			
Technical Paper Preparation												E			
Viva Preparation													F		
Final Dissertation (Hardcopy) Preparation															G

Milestone	Mark	Date
Progress Report	A	9-Nov
Pre-Sedex	B	30-Nov
Draft Final Report	C	1-Dec
Dissertation (Soft bound)	D	7-Dec
Technical Paper	E	9-Dec
Viva	F	16-Dec
Dissertation (Hardbound)	G	12-Jan

CHAPTER 4

RESULTS & DISCUSSION

4.1 SARA Fractions

The composition of saturates, aromatics, resins and asphaltenes in crude oil are analyzed to represent the oil composition. The interaction between the components are to be analyzed to help explain the applicability to Heithaus parameters and Hildebrand solubility parameters. Based on weight calculation and measurement from HPLC, different SARA are shown in the figure 4.1 below.

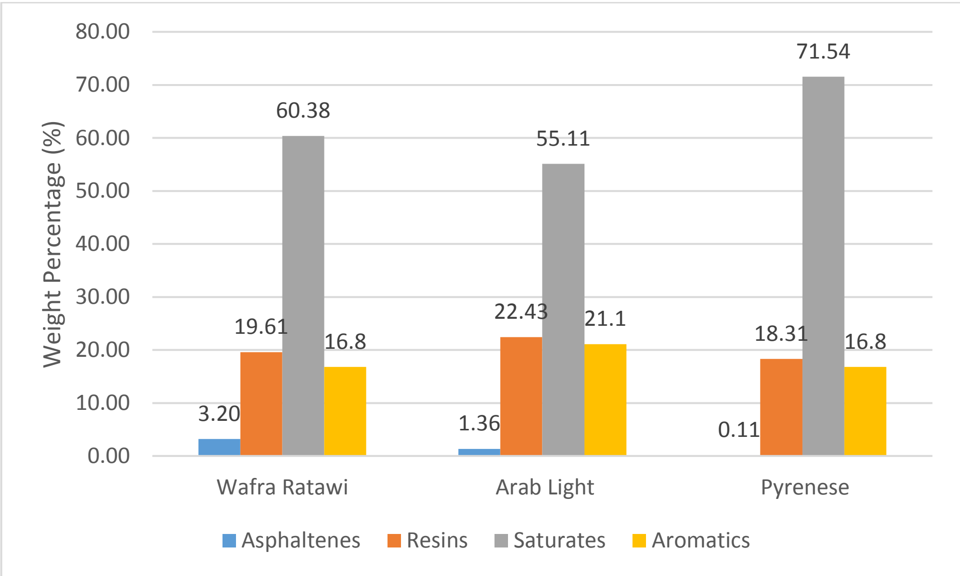

Figure 4. 1 SARA fractions analysis for three different crude oils

From the figure, Arab Light is seemed to contain the highest amount of resins compared to other crude oil at 22.43 wt%. Wafra Ratawi is proved to be containing the highest amount of asphaltenes fractions, which is supported by the crude assay analysis in on each crude oil. Pyrenese contains almost no asphaltenes condition which is at 0.11 wt%. For saturates, Pyrenese is roughly analyzed to contain more saturates compared to Ratawi and Arab Light. In the range of 10 to 21, aromatics would be the second most composited fractions in all types of oil.

4.2 Heithaus Parameters Analysis

Based on the SARA measurement, the effect of each components to the different parameters and the relation with different carbon numbers of titrant explained together under Heithaus Parameter Analysis.

4.2.1 Pa parameter

Pa parameter is defined as the peptizability of asphaltenes in oil system. The higher the Pa, the higher the peptizability which indicates stronger association among asphaltenes colloids in the system. In stable oil, asphaltenes are well peptized by maltenes. Colloidal asphaltenes tend to be in dissolved state due to resins avoiding large asphaltenes aggregates to occur. (Zubair et al. 2015).

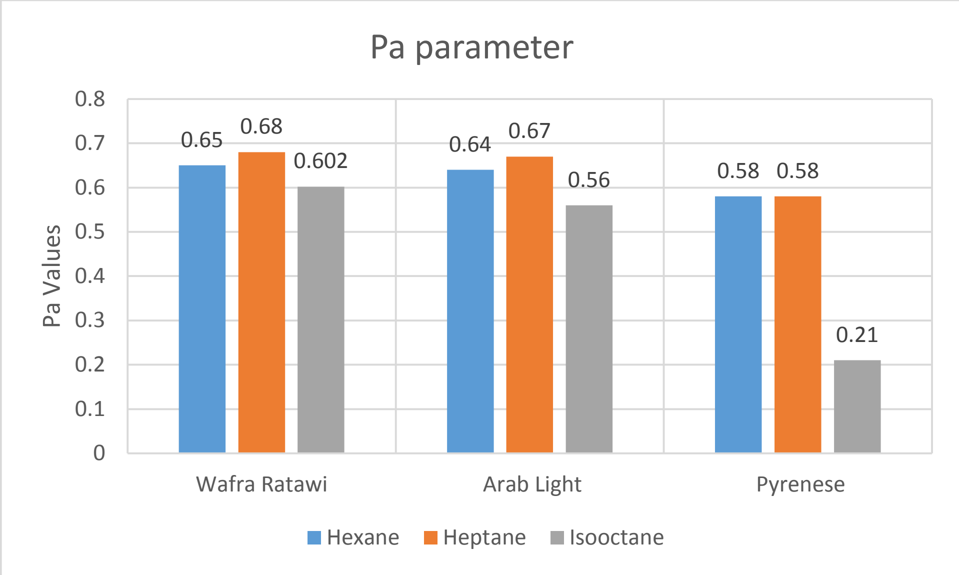

Figure 4. 2 Pa parameters for all conditions

Figure 4.2 shows the Pa parameter for different conditions based on different crude oil and titrants used. In the aspect of different crude oil, Pa is higher for Pyrenese followed by Arab Light and Ratawi in overall. Higher Pa shows asphaltenes are less likely to aggregate in noticeable manner. Figures 4.3 shows the amount of resins and asphaltenes fractions in each crude oil.

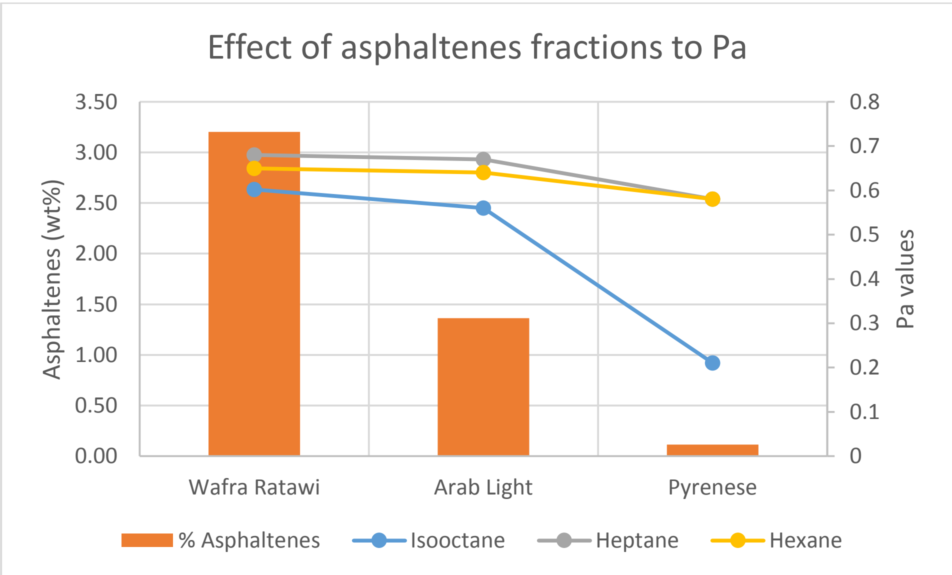

Figure 4. 3 Relationship between asphaltenes fractions and Pa

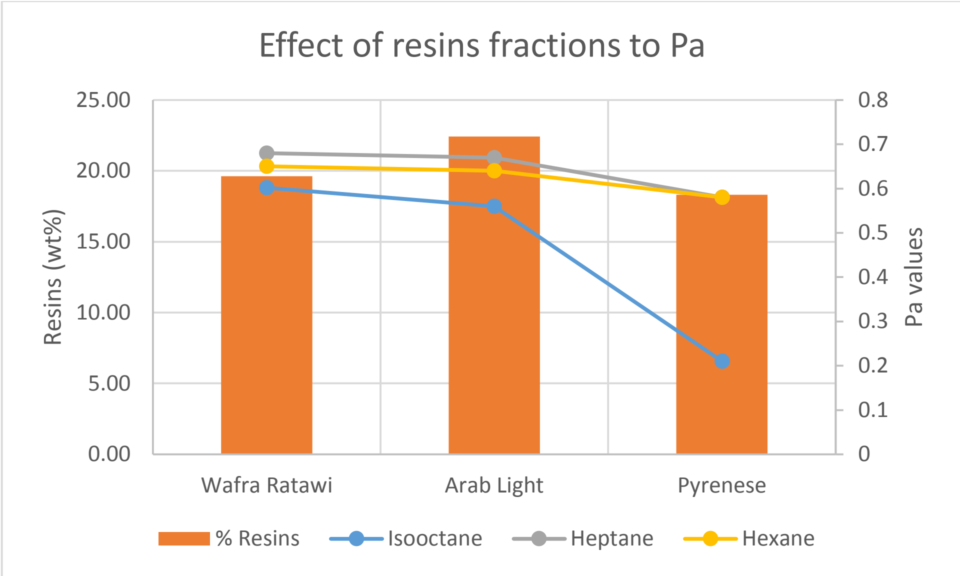

Figure 4. 4 Relationship between resins fractions and Pa

Figure 4.3 and 4.4 above show distribution of asphaltenes and resins fractions for all types of oil used in relation to the Pa parameters for different conditions. The trend for asphaltenes fractions are in linear relationship with Pa values. However, even with huge differences in asphaltenes composition, Pa values for Ratawi and Arab Light are vague. This might explain on the little contribution of asphaltnenes towards asphaltenes precipitation. In the aspect of different titrants used, isooctane produces different Pa values trend compared to hexane and heptane. This might be due to larger difference in properties of isooctane compared to hexane and heptane in terms of carbon numbers and structure.

The effect of resins may explain on the similar behavior of Pa values for Ratawi and Arab Light. The higher fraction of resins for Wafra Ratawi may increase the peptizability of asphaltenes in oil system, making asphaltenes have stronger associations with other components in oil. For Pyrenese, lower asphaltenes fraction does not directly indicate higher Pa. The lower amount resins indirectly affecting the lesser peptizability for Pyrenese system.

Asphaltenes and resins fractions have shown effects to Pa values. Saturates are said to be contributive to precipitation on several studies. On the other side, aromatics fractions have not been mentioned in the study of oil composition.

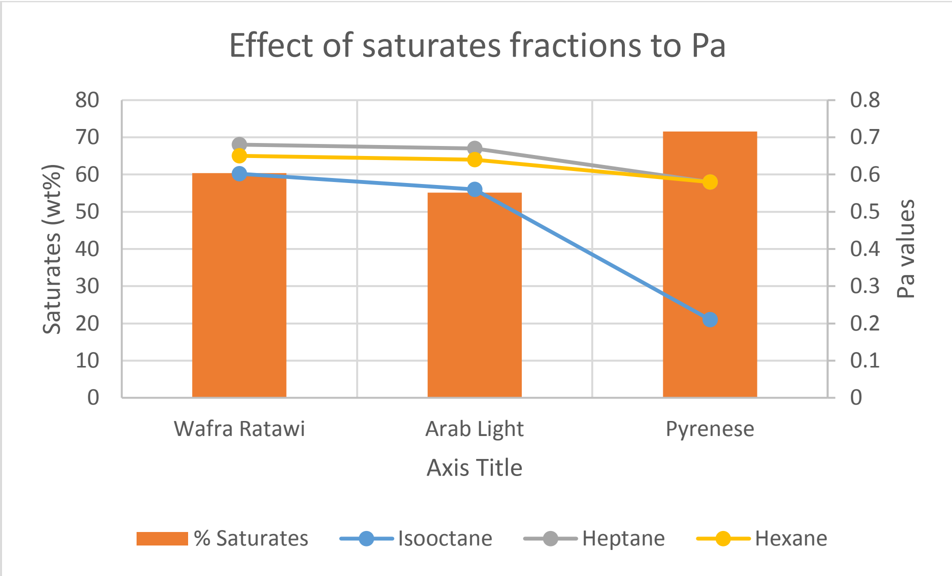

Figure 4. 5 Relationship between saturates fractions and Pa

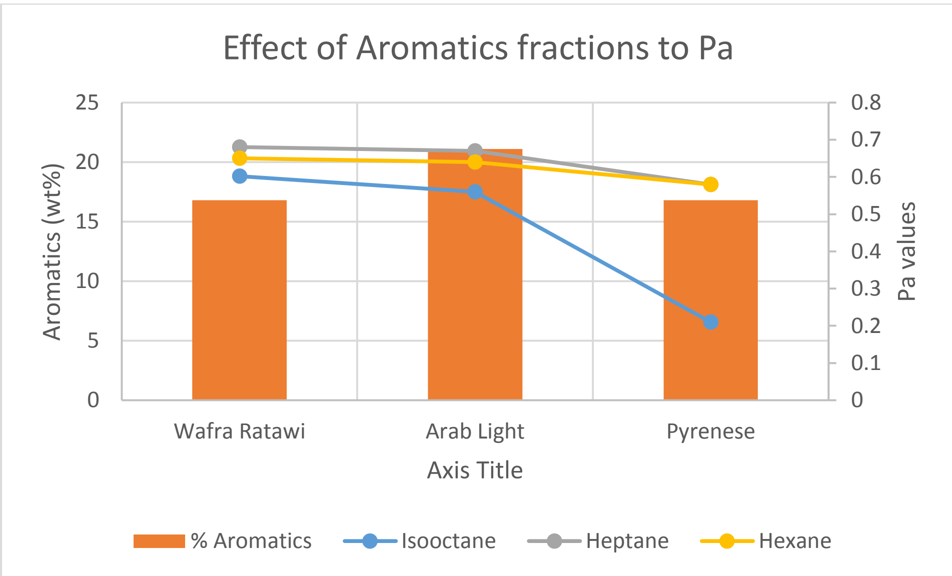

Figure 4. 6 Relationship between aromatics fractions and Pa

Figures 4.5 and 4.6 above show the effect of saturates and aromatics to Pa parameter. As saturates increase, the Pa values decrease for all conditions. Decreasing Pa values proves the low peptizability of asphaltenes making weak interactions between components. Saturates are nonpolar, making it stable on their own. For Pyrenese, having high saturates might not help to avoid asphaltenes precipitation. As for aromatic fractions, there is not much distinction between different crude oil.

4.2.2 Po parameter

Po parameter defines the solvency of asphaltenes in oil system. Higher value of Po is explained by the increasing solvating power of maltenes in oil. The stronger the solvating power of maltenes, the lesser the possibility of asphaltenes to start forming aggregates, thus precipitation is less likely to occur. Figure 4.7 below shows the Po parameter for different conditions.

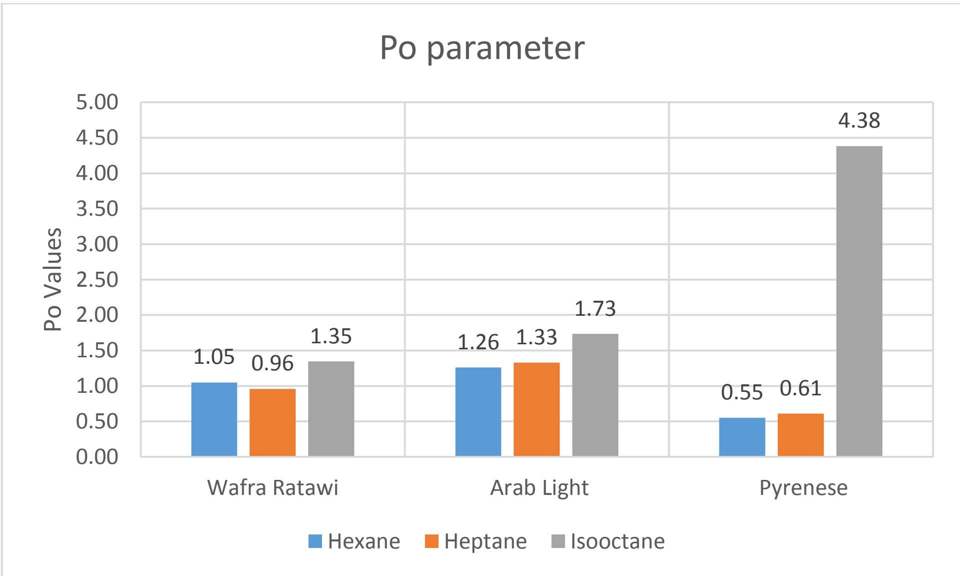

Figure 4. 7 Po parameter for all conditions

Figure above indicates increasing trend for Po parameters for Arab Light and Pyrenese. Increasing trend indicates increasing solvency characteristic of asphaltenes inside maltenes. For all crude oil, Po is the highest by using isooctane. There is no concise trend observed for different crude oil used, but Ratawi and Arab Light have constant and higher Po compared to Pyrenese.

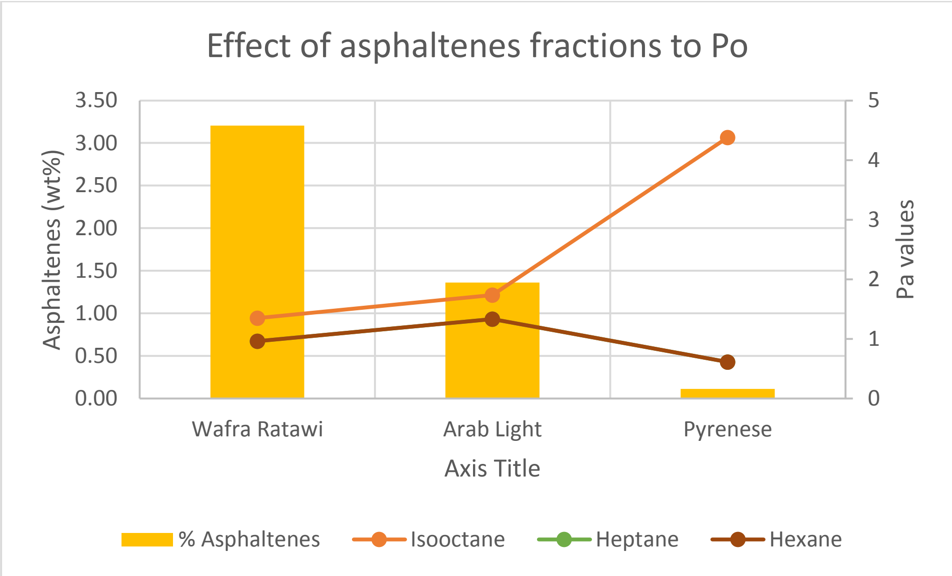

Figure 4. 8 Relationship between asphaltenes fractions and Po

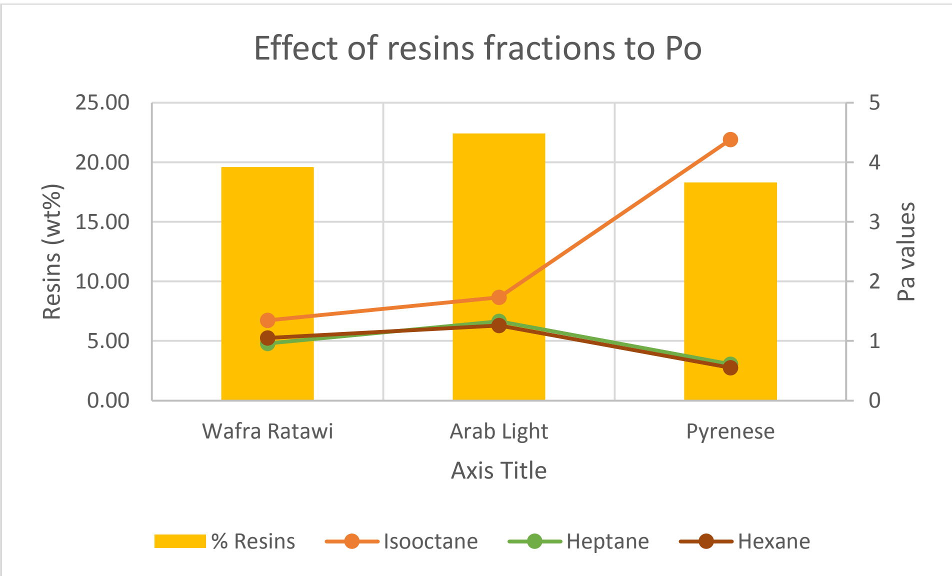

Figure 4. 9 Relationship between resins fractions and Po

As the asphaltenes fractions decrease, the Po tends to increase for isooctane. However, for heptane and hexane, they do not have specific trend other than having higher Po at Arab Light which contains asphaltenes fractions at higher and lower than other oil. This explains on the same concept with Pa values where the contribution of asphaltenes fractions toward solvency characteristics of asphaltenes in oil are not reliable.

The higher the resins fractions, the higher the Po parameters for hexane and heptane. This explains on the effect of resins to asphaltenes precipitation. Having more resins to associate with asphaltenes allow asphaltenes to dissolve in oil thus the solvent like characteristic. Isooctane has a different trend for resins effect. Similarly, the carbon number effect of titrant do not show constant trend to the precipitation.

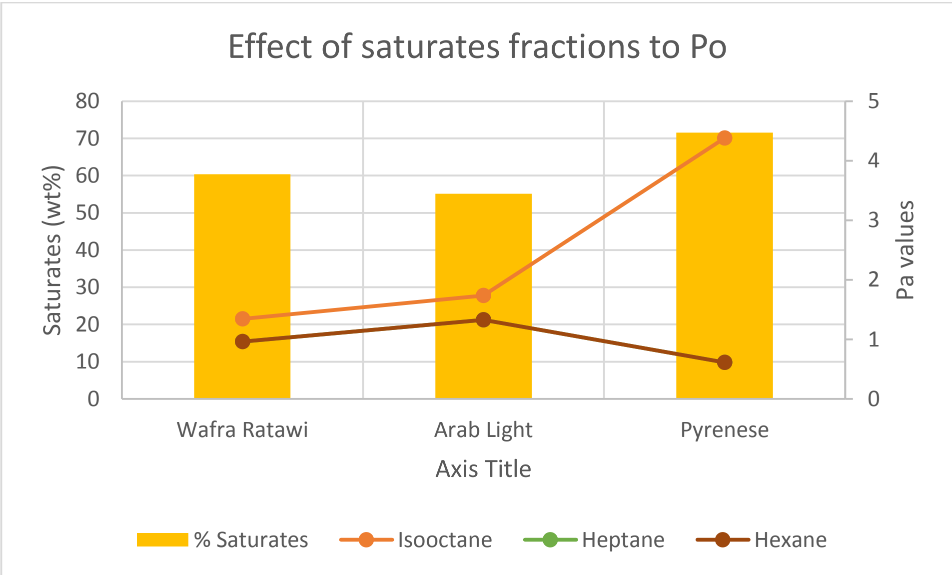

Figure 4. 10 Relationship between saturates fractions and Po

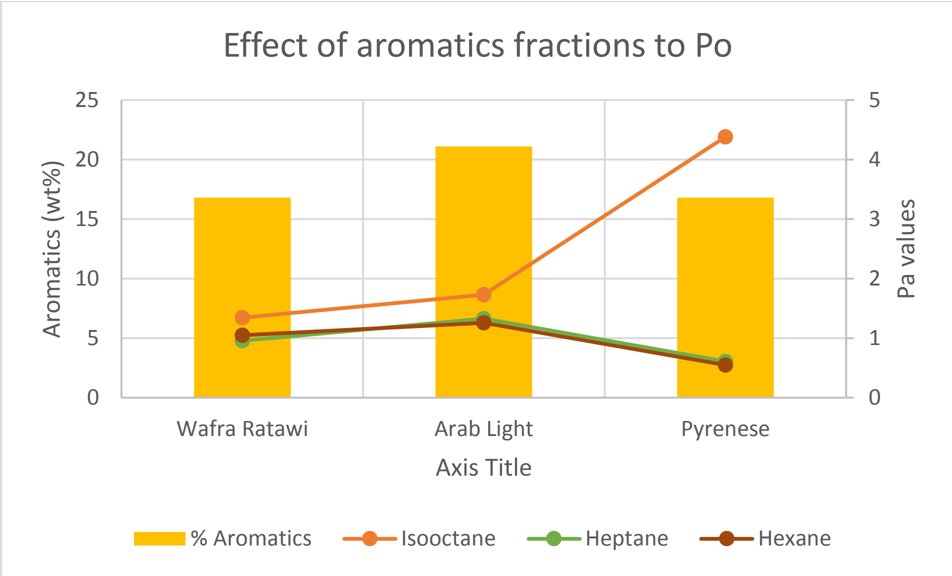

Figure 4. 11 Relationship between aromatics fractions and Po

Figures 4.10 and 4.11 above show clearly the effect of having saturates causing low solvency characteristics of asphaltenes, however, isooctane shows contradicting behavior. Again, this might be explained by the characteristic of the isooctane itself. Having different structure and properties compared to hexane and heptane may be the cause to behave differently. Having greater amount of aromatics for Arab Light do not help to increase the dispersion forces for asphaltenes, therefore Po parameters show typical values compared to others.

4.2.3 P Parameter

P parameter is the overall stability of colloidal suspension of oil. This measurement shows certain degree of measurement of oil and asphaltenes to remain in stable state. As stated earlier, typical value of P would be 2.5 to 10. Any system below 2.5 is considered to be very unstable and weak in ensuring stability. Having a stable system should provide difficult environment for asphaltenes to start aggregate and causing precipitation.

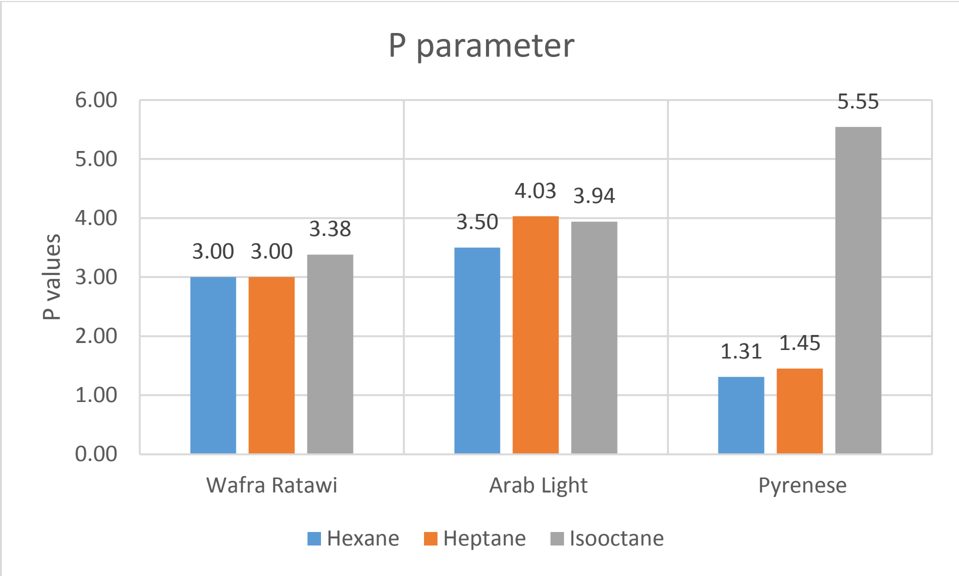

Figure 4. 12 P parameter for all conditions

Figure 4.12 above shows non-uniform pattern of P values for different crude oil and titrant. In overall, Ratawi and Arab Light have stable systems based on the higher P values. At condition titrated with isooctane, P would be greater for Ratawi and Pyrenese. The pattern is different for Arab Light condition throughout different titrant.

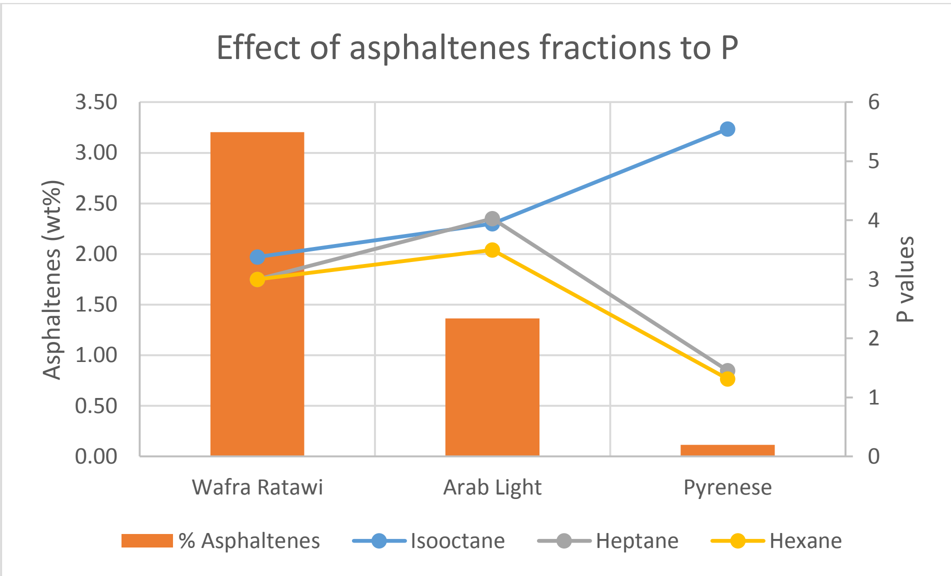

Figure 4. 13 Relationship between asphaltenes fractions and P

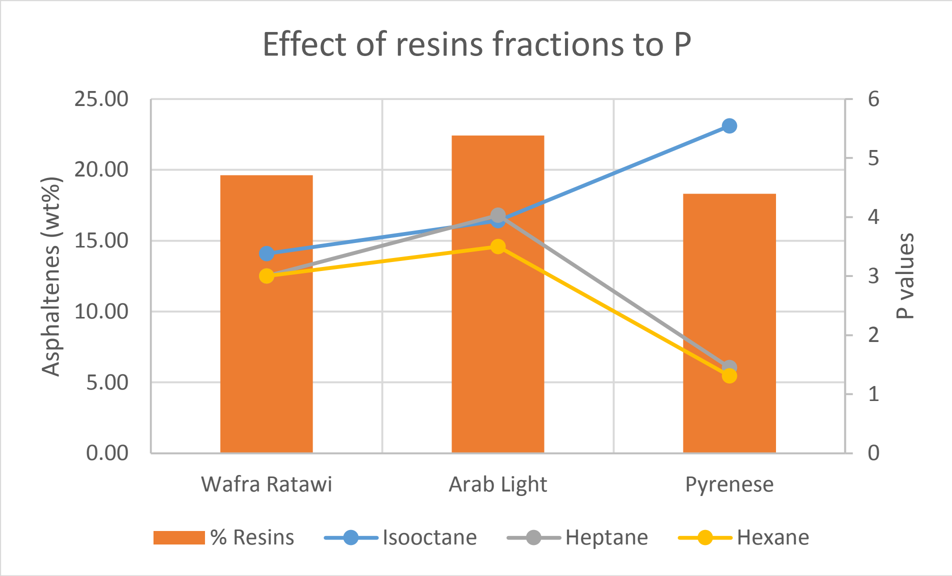

Figure 4. 14 Relationship between resins fractions and P

Similarly to Po parameter, increasing amount of asphaltenes do not give decreasing trend of P values. Additionally, increasing carbon number do produce increasing trend of P values either. These prove on the significance of other components of oil that effect asphaltenes precipitation at higher degree. The overall stability parameters are commonly higher at Arab Light having the second most asphaltenes fractions for hexane and heptane conditions. However, it is seemed more stable for Pyrenese titrated with isooctane.

Referring to resins fractions, it explains on the behavior of P values being higher at Arab Light. At Arab Light, resins are more in percentage making asphaltenes in stable condition. The very low P values for Pyrenese can somehow be supported by the little amount of resins contained, however, the huge difference may require other analysis to strengthen the result. In overall, the amount of resins give more significant relation to the asphaltenes precipitation through different parameters.

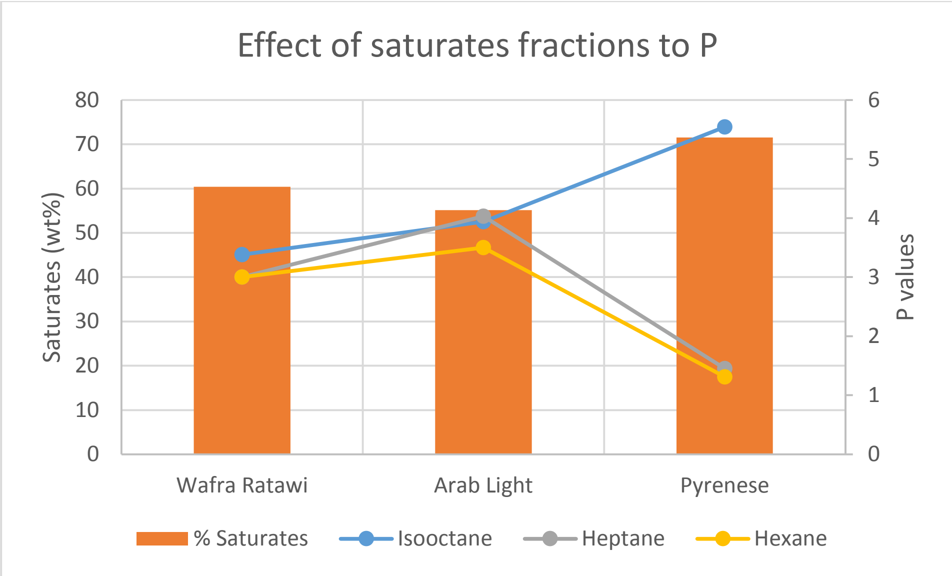

Figure 4. 15 Relationship between saturates fractions and P

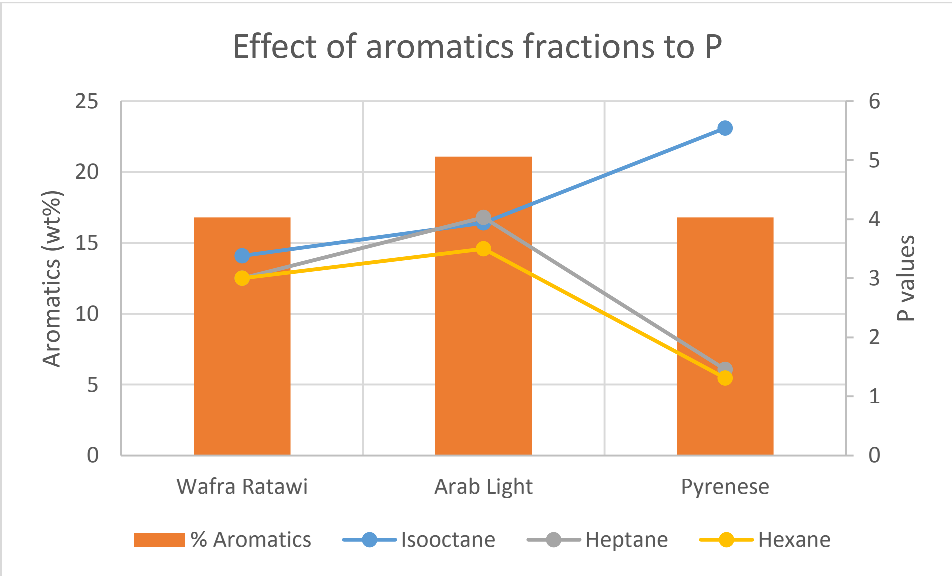

Figure 4. 16 Relationship between aromatics fractions and P

Based on figures 4.15 and 4.16 above, Pyrenese have very low overall stability of colloidal suspension of oil for heptane and hexane. It is reasonable due to high amount of saturates. Having a slightly higher P parameter for Arab Light also indicates lower saturates fraction.

4.3 Hildebrand's Solubility Parameter

Hildebrand's solubility parameter simply indicates the solubility degree of components in the overall system. The higher the values, the higher the solubility degree of components. Thus, creating a difficult environment for asphaltenes to start precipitate.

4.3.1 δ_{oil}

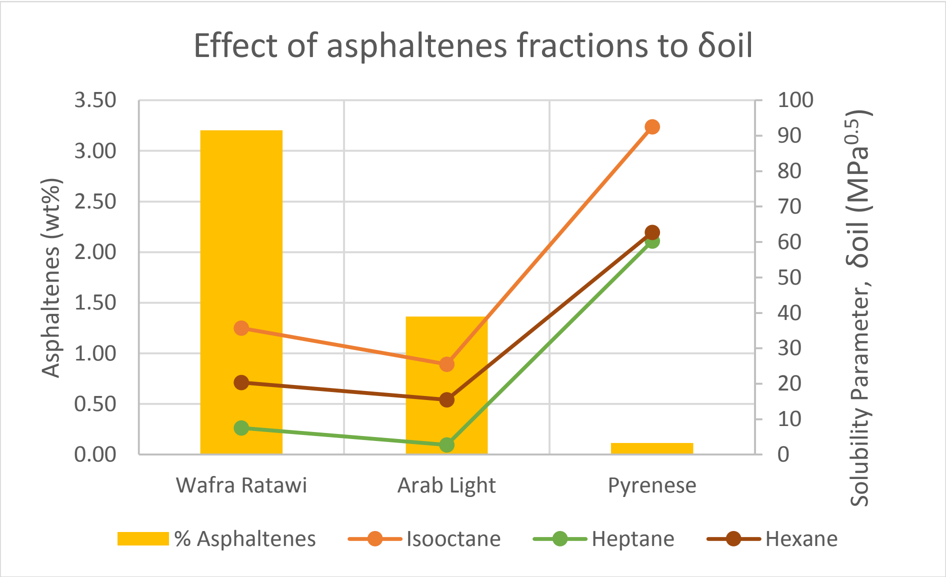

Figure 4. 17 Relationship between asphaltenes fractions and δ_{oil}

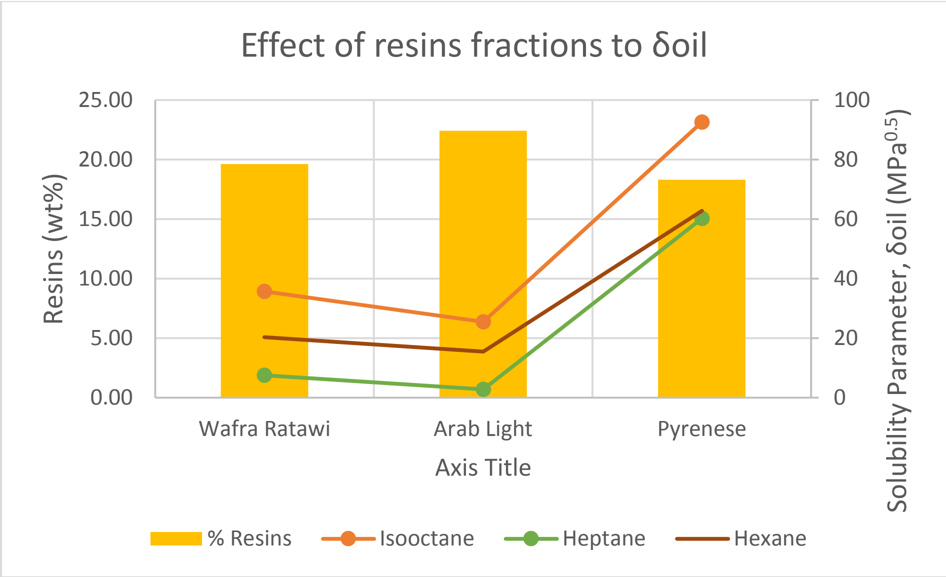

Figure 4. 18 Relationship between resins fractions and δ_{oil}

From the figures 4.17 and 4.18 above, δoil is the highest at Pyrenese, followed by Wafra Ratawi and Arab Light. δ_{oil} is also higher for isooctane, followed by hexane and heptane. Referring to effect of asphaltenes fractions, as the amount decreases, the solubility increases. This is reasonable as it proves a study on the effect of asphaltenes composition to precipitation. Oil with more asphaltenes composition will promote asphaltenes precipitation. So Pyrenese with the least asphaltenes fractions should be more stable as a system. In the aspect of titrant, increasing carbon number of titrant do not give increase δ_{oil}.

Referring to the effect of resins fractions toward δ_{oil}, δ_{oil} is lowest at Arab Light despite having the highest resins content followed by Wafra Ratawi and Pyrenese. This behavior may be caused by other factors that are considered in the calculation of δoil. The interaction between the titrant, the oil and flocculation ratio can be discussed. δmix for different condition differ. At Arab Light, the δmix and the FRmax are higher. Higher FRmax indirectly relates to onset point. The time taken for precipitation to start occur may be longer. Therefore, the contradicting relations between different values may help to lead to different compositional effect.

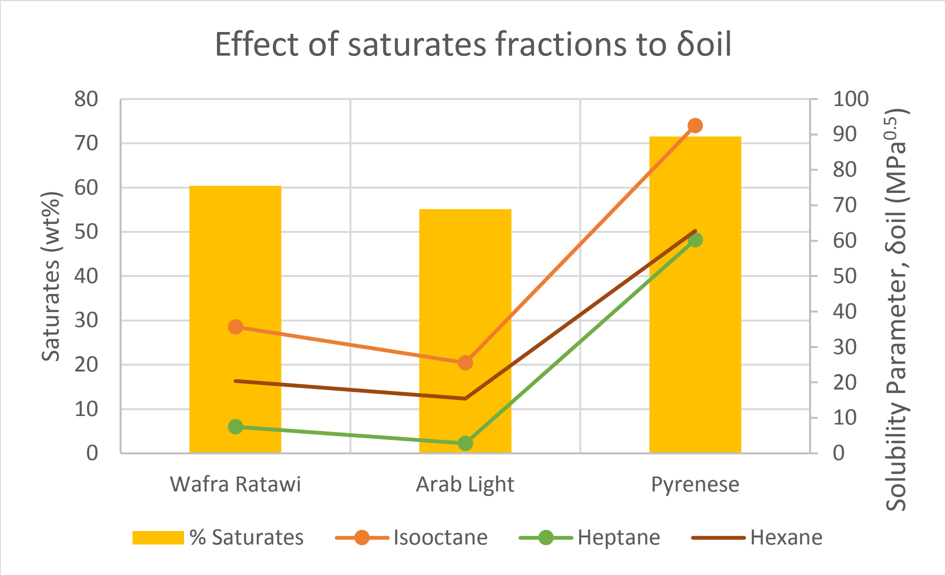

Figure 4. 19 Relationship between saturates fractions and δ_{oil}

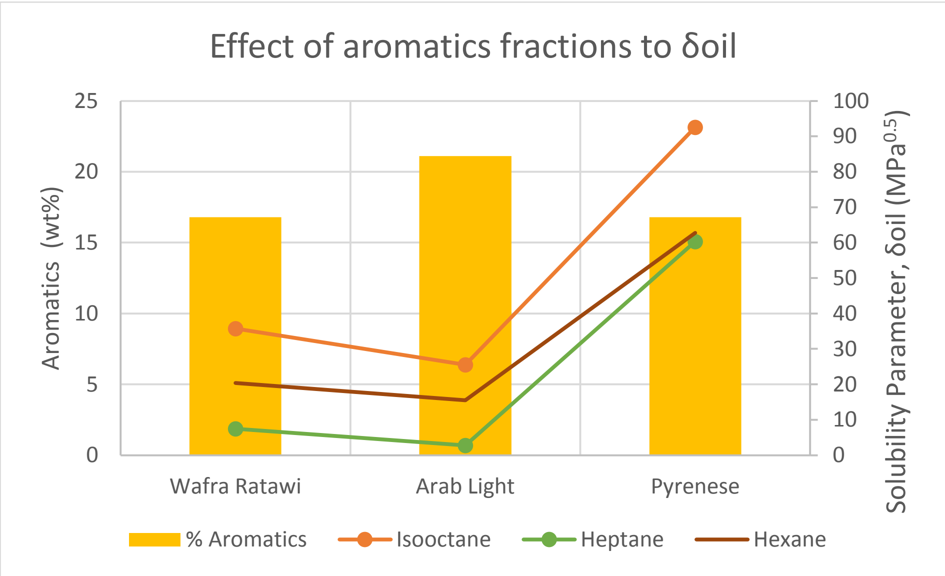

Figure 4. 20 Relationship between aromatics and δ_{oil}

Based on the figures 4.19 and 4.20 above having high saturates amount do not reflect the high solubility of the system which contradicts with the Heithaus Parameters Analysis. For Hildebrand's solubility parameter, the consideration of titrant used, solvent solubility, and the flocculation ratio create more detailed interaction between different aspects. The oil itself may not be as solvent like which may not directly affect the asphaltenes precipitation behavior.

4.3.2 δ_{as}

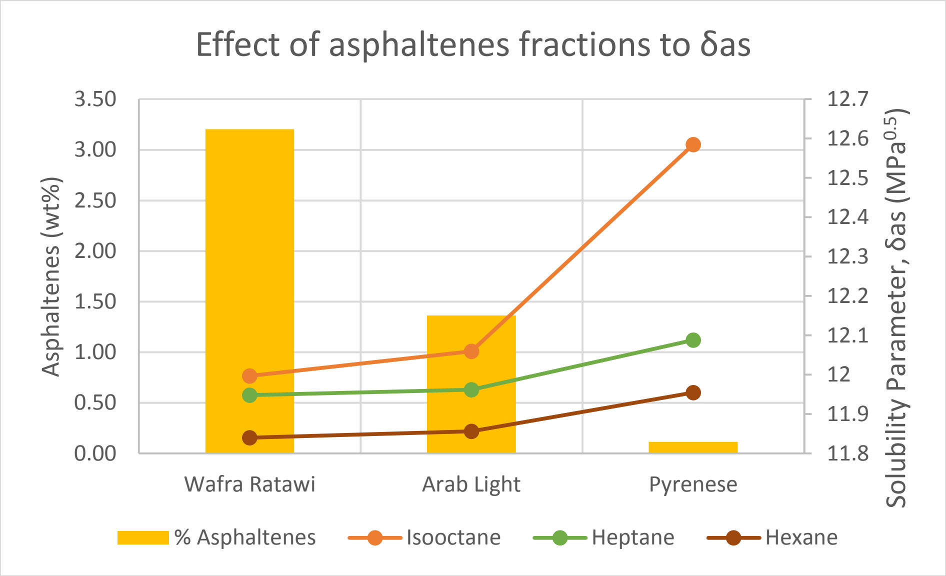

Figure 4. 21 Relationship between asphaltenes fractions and δ_{as}

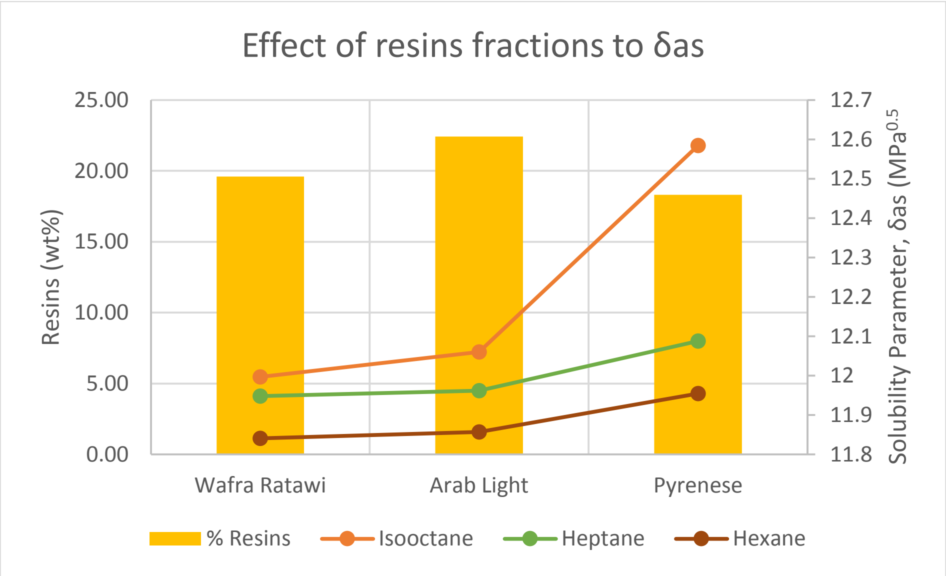

Figure 4. 22 Relationship between resins fractions and δ_{as}

The two figures 4.21 and 4.22 show the δas relation with respect to asphaltenes and resins fractions and different titrants. The higher the δas, the higher the solubility of asphaltenes in crude oil. The higher solubility of asphaltenes, the better the interaction with other components causing less possibility of precipitation. For both resins and asphaltenes fractions, the trend is the same for δas. The resins and asphaltenes may not have strong impact on the solubility condition of asphaltenes with respect to the system.

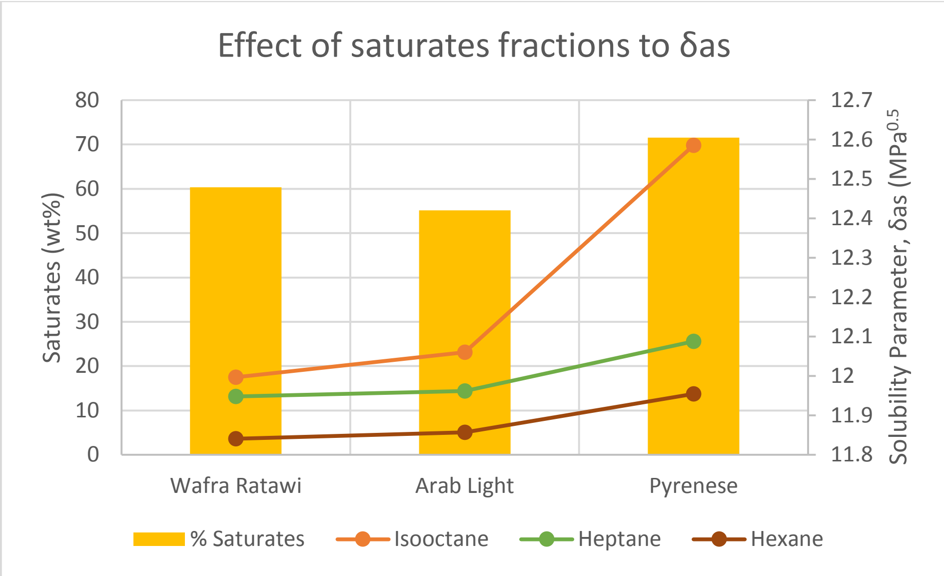

Figure 4. 23 Relationship between saturates fractions δ_{as}

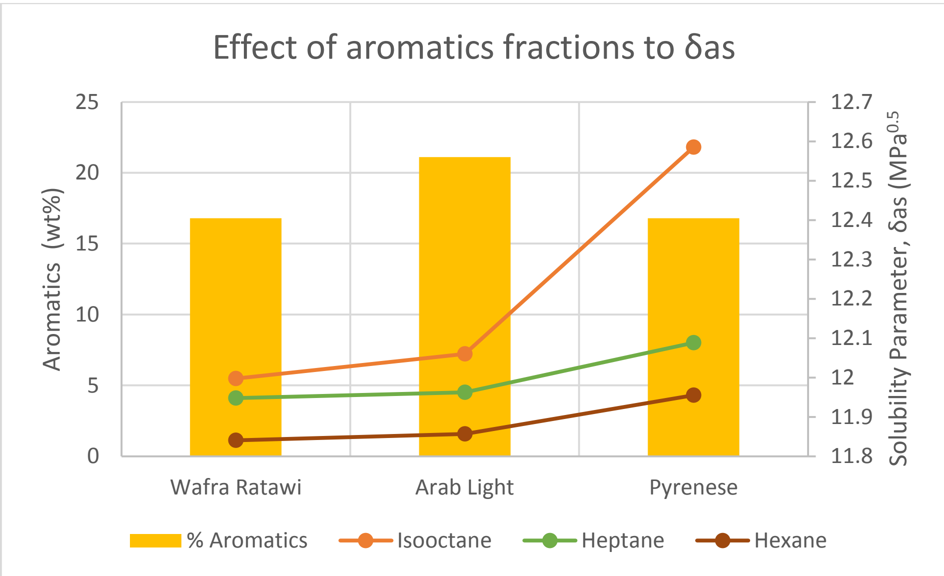

Figure 4. 24 Relationship between aromatics fractions and δ_{as}

Similar trend with δ_{oil}, δ_{as} on saturates and aromatics fractions show linear relationship, which is the opposite of in Heithaus Parameters Analysis. Different other factors may be the cause of the behavior as well as lack of reliability of the results used to represent δ_{as}.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 Conclusion

The Heithaus parameters and Hildebrand's solubility parameters are used to analyze the effects of oil composition and different titrant. In general, some of the theories on the effect of oil composition are proved. One theory is on the effect of asphaltenes fractions to asphaltenes precipitation. The higher the asphaltenes fractions, the higher the asphaltenes precipitation possibilities. However this has not been approved to every condition. This concept has to be supported by the effects of resins and saturates for the most. Condition with high resins provide stable and high solubility of oil system. The functions of resins are significant to keep association between asphaltenes. High saturated condition cause low stability to system by referring to Pa, Po, and P. Hildebrand solubility parameters help to support the Heithaus parameter analysis.

In the aspect of the effect of titrant the comparison is done based on different carbon numbers. Isooctane having higher carbon number might be the one major characteristic in allowing high solubility of asphaltenes. However, this has not been consistent for all condition. Hexane and heptane produce similar patterns for all conditions. This can be explained based on their closed properties including carbon number.

5.2 Recommendation

- Other properties of crude oil can be included in investigation to further strengthen any inconsistency in the results. (ie. Metal composition, API gravity and viscosity)
- Additional result analysis method can be added to further prove and support analysis done other than Heithaus Test method and Hildebrand's solubility parameters
- The characteristics of titrants should be defined other than the carbon number of n-alkanes

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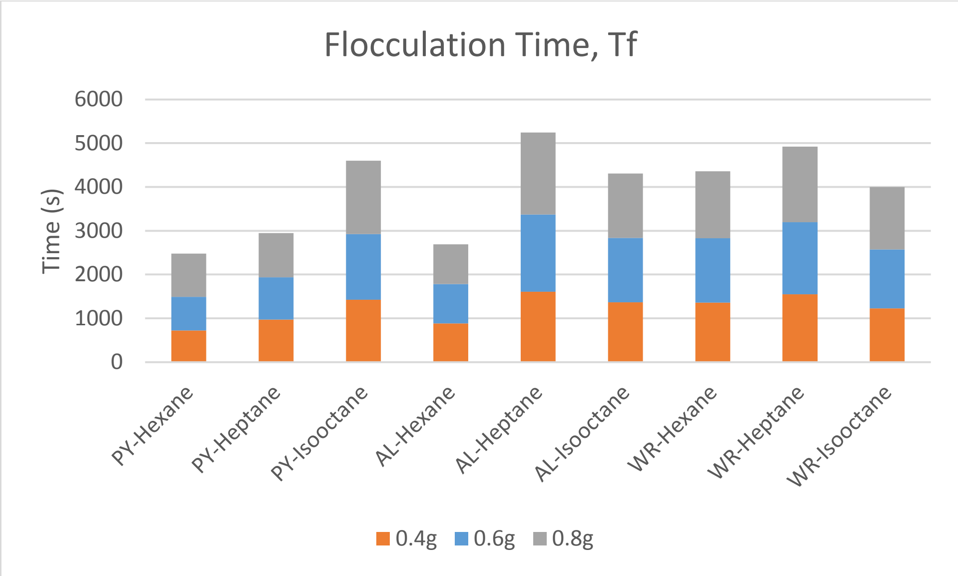
APPENDICES

a. Flocculation onset points



b. FRmax and Cmin

Al-hep	Caverage	FRaverage
0.4	0.038764	0.287456
0.6	0.054395	0.269398
0.8	0.069221	0.257581
Intercept	0.33	0.33
PY-hep	Caverage	FRaverage
0.4	0.054418	0.401577
0.6	0.081478	0.403641
0.8	0.105297	0.391585
Intercept	2.2	0.42
WR-hexane	C	FR
	0.04374	0.323745
	0.061715	0.306433
	0.079974	0.297951
	0.5	0.35
AL-hexane	C	FR
	0.042321	0.313649
	0.065437	0.301813
	0.074996	0.279201
	0.4	0.36

PY-hexane	C	FR
	0.057259	0.424352
	0.090771	0.41866
	0.112045	0.417126
	3.2	0.42
PY-isooctane	Caverage	FRaverage
0.4	0.064688	0.47421
0.6	0.093118	0.46047
0.8	0.106892	0.396823
Intercept	0.22	0.79
WR-isooctane	Caverage	FRaverage
0.4	0.047134	0.346975304
0.6	0.066033	0.326063147
0.8	0.083913	0.313017324
Intercept	0.42	0.398
Al-isooctane	Caverage	FRaverage
0.4	0.043605	0.321969
0.6	0.061982	0.306743
0.8	0.082554	0.307063
Intercept	0.34	0.44
WR-hep	Caverage	FRaverage
0.4	0.040052	0.295337
0.6	0.056876	0.281158
0.8	0.073591	0.273875
Intercept	0.5	0.32