

**INVESTIGATION OF ASPHALTENE AGGREGATION KINETICS IN THE
PRESENCE OF WATER-IN-OIL EMULSION**

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
Case Western Reserve University, and Institut Français du Pétrole
2017

บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)
เป็นแฟ้มข้อมูลของนิสิตเจ้าของวิทยานิพนธ์ที่ส่งผ่านทางบัณฑิตวิทยาลัย

The abstract and full text of theses from the academic year 2011 in Chulalongkorn University Intellectual Repository (CUIR)
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Thesis Title: Investigation of Asphaltene Aggregation Kinetics in the Presence of Water-in-Oil Emulsion
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ABSTRACT

5871014063: Petrochemical Technology Program

Penpitcha Roengsamut: Investigation of Asphaltene

Aggregation Kinetics in the Presence of Water-in-Oil Emulsion

Thesis Advisors: Asst. Prof. Pomthong Malakul, and Prof. Scott H.

Fogler 54 pp.

Keywords: Asphaltene/ Asphaltene aggregation/ Emulsified water in oil/ Rate of asphaltene aggregation

Asphaltene is a component of the petroleum liquid defined operationally. It represents the most refractory (or the heaviest fraction). It is well-known that changes in temperature, pressure, or composition can destabilize asphaltenes and cause aggregation and deposition in porous formations, production lines, and processing facilities (Sheu and Mullins 1995). This leads to the study of the behavior of asphaltene aggregation and parameters that could affect the rate of aggregation which, in this case, is water-in-oil emulsion. In addition, the asphaltene aggregation model derived by Haji-Akbari (2013) is applied as a framework in this study which explains the correlation between the time when asphaltene starts aggregating and the important parameters such as viscosity, collision efficiency and initial concentration of asphaltene nanoparticles. The experimental procedure developed by Tabish (2009) is also utilized as a standard procedure for every detection time experiment (the addition of heptane in oil and the aging method) and able to plot the aging time as a function of heptane concentration. As a consequence, the graph shows the rate of asphaltene aggregation comparing between the oil and water in oil. From this graph, it is shown that there are 2 controversial trends regarding 2 different water concentrations in oil. At lower water concentration (1wt% water), the rate of asphaltene aggregation becomes faster but, on the other hand, the rate is slowed down with higher water content (10wt% water). With these results, it can be concluded that water has effect on the rate of asphaltene aggregation.

บทคัดย่อ

เพ็ญพิชชา เรืองสมุทร : การศึกษาอัตราการเกิดการตกตะกอนของแอสฟอลทีนโดยมีน้ำเป็นส่วนประกอบ (Investigation of Asphaltene Aggregation Kinetics in the Presence of Water-in-Oil Emulsion) อ. ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร.ปมทอง มาลากุล และ ศาสตราจารย์ สก็อต ฟอล์กเลอร์ 54 หน้า

แอสฟอลทีนเป็นของเหลวที่มาจากกระบวนการผลิตปิโตรเลียม เป็นวัสดุที่หนืดมากที่สุด (หรือส่วนที่หนักที่สุด) และเป็นที่ยึดกันดีว่าเมื่อการเปลี่ยนแปลงในอุณหภูมิ ความดันหรือองค์ประกอบสามารถทำให้แอสฟอลทีนเกิดความไม่เสถียรและก่อให้เกิดการรวมตัวและการสะสมในท่อสายการผลิตและในโครงสร้างการผลิตอื่นๆ (Sheu และ Mullins 1995) จากการศึกษาเรื่องแอสฟอลทีนนี้นำไปสู่การศึกษาพฤติกรรมของการรวมตัวของแอสฟอลทีนและปัจจัยที่อาจส่งผลกระทบต่ออัตราการรวมตัวของแอสฟอลทีน ซึ่งในกรณีนี้คืออิมัลชันของน้ำในน้ำมัน นอกจากนี้รูปแบบการรวมของแอสฟอลทีนที่ได้มาโดย Haji-Akbari (2013) จะถูกนำไปใช้เป็นการรอบในกระบวนการศึกษานี้ด้วย ซึ่งสามารถอธิบายความสัมพันธ์ระหว่างเวลาเมื่อแอสฟอลทีนเริ่มรวมตัวและตัวแปรที่สำคัญเช่นความหนืด ประสิทธิภาพการชนกันระหว่างอนุภาคของแอสฟอลทีน และความเข้มข้นเริ่มต้นของอนุภาคแอสฟอลทีน ในส่วนของขั้นตอนการทดลอง ได้มีการพัฒนาโดย Tabish (2009) และถูกนำมาใช้เป็นขั้นตอนมาตรฐานสำหรับการทดลอง (การเติมเฮปเทนและวิธีการปล่อยให้ขนาดอนุภาคมีขนาดใหญ่ขึ้น) และการพล็อตกราฟระหว่างเวลาและความเข้มข้นของเฮปเทน ซึ่งกราฟนี้จะแสดงให้เห็นถึงอัตราการรวมแอสฟอลทีนเปรียบเทียบระหว่างน้ำมันและน้ำมันที่มีน้ำเป็นส่วนผสม เมื่อพล็อตแล้วจะเห็นว่ามีการพหุนามเชิงเส้น ความเข้มข้นของน้ำที่แตกต่างกันให้ผลต่างกัน ในระบบที่มีน้ำความเข้มข้นต่ำกว่า (1wt%) อัตราของการรวมแอสฟอลทีนจะเพิ่มขึ้นแต่ในทางกลับกันอัตราจะชะลอลงเมื่อปริมาณน้ำสูงขึ้น (10wt%) จากผลเหล่านี้สามารถสรุปได้ว่าน้ำมีผลต่ออัตราการรวมตัวกันของแอสฟอลทีน

ACKNOWLEDGEMENTS

First and above all, the author would also like to thank Prof. Scott H. Fogler and Asst. Prof. Pomthong Malakul Na Ayudhaya for accepting me as one of the research group members at the University of Michigan, also their encouragement, guidance, critical comments, and correction of the thesis.

I want to express my deep thanks to my esteemed Ph.D. students from Prof. Fogler group, Claudio Vilas Boas Favero and Luqman Hakim Bin Ahmad Mahir, for the trust, the insightful discussion, offering valuable advice, and infinite support during the whole period of the study, and especially for their patience and guidance during the presentation and writing process. Without their passionate participation and input, this thesis could not have been successfully conducted.

The author is grateful for the scholarship and funding of the thesis work provided by the Petroleum and Petrochemical College; and the Center of Excellence on Petrochemicals and Materials Technology.

Finally, I must express my very profound gratitude to my parents for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them.

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ABBREVIATION

IAA	Interfacially active asphaltene
HSP	Hansen solubility parameter
RI	Refractive index

LIST OF SYMBOLS

δ	Solubility parameter
δ_{asph}	Solubility parameter of asphaltene
δ_{sol}	Solubility parameter of solution
V	Molar volume of the pure solvent
E	Energy of vaporization,
C	Cohesive energy density
ΔH	Heat of vaporization
R	Gas constant
T	Temperature
E_D	Dispersion cohesive energy
E_P	Polar cohesive energy
E_H	Hydrogen bonding cohesive energy
FRI	Function of refractive index
C_i	Concentration of particles of size i
K_{ij}	Collision kernel for aggregation
k_B	Boltzmann constant

CHAPTER I

INTRODUCTION

Asphaltene is a component of the petroleum liquids defined operationally. It represents the most refractory (or the heaviest) fraction. A generally accepted definition of asphaltenes is by their solvent solubility. The fraction insoluble in heptane (or pentane) but soluble in toluene is called asphaltene. In addition to the non-refinerable nature, asphaltene has been known to initiate wellbore plugging, pipeline deposition; hinder the refining yields, and initiate coking and so on. Such hindrances on production and processing have made asphaltene one of the most focused materials in petroleum research (Sheu and Mullins, 1995).

As mentioned in previous paragraph, asphaltene is an undesirable component and it is necessary to be removed from the petroleum processing facilities. Also, the remediation and prevention of asphaltene deposits are costly and, the mechanism of asphaltene destabilization is poorly understood. Many researches have been conducted in order to understand the behavior of asphaltene and able to applied to the actual situation in the oil and gas industries. From Maqbool *et al.* (2011), asphaltene deposits in the petroleum facilities are explained to likely begin with asphaltene destabilization due to thermodynamic factors such as changes in the temperature, pressure loss during production, or changes in the composition of fluid during enhanced recovery operations, such as CO₂ flooding, acid stimulation, and mixing of crude oil with diluents and other oils. Once asphaltenes destabilize, they tend to aggregate. Another study from Haji-Akbari *et al.* (2013) has mentioned the definition of destabilization that it is referred to both the phase separation or increase in aggregation tendency of nanoparticles and the subsequent collision and eventual aggregation of asphaltene nanoparticles into aggregates that are detectable under optical microscopy (precipitation).

Knowing that change in compositions in petroleum fluid extracted from reservoir can have some influences, water is one component that could not be taken for granted. Emulsions of crude oil and water can be encountered at many stages during drilling, producing, transporting and processing of crude oils and in many locations such as in hydrocarbon reservoirs, well bores, surface facilities,

transportation systems including refineries (Langevin *et al.*, 2004). However there are still many unsolved questions related to the peculiar behavior of these emulsions.

From many studies, it is realized that if there is a change in composition, then there might be a possibility that water which is one of the component coming along with the petroleum production has some effect on the rate of asphaltene aggregation. Therefore, this leads to the primary goal of this study which is to investigate rate of asphaltene aggregation with the presence of water. In addition, the asphaltene aggregation model derived by Haji-Akbari *et al.* (2013) will be applied to the study as a framework as well.

CHAPTER II

LITERATURE REVIEW

2.1 Petroleum Crude Oil

Petroleum and the equivalent term crude oil cover a wide assortment of materials consisting of mixtures of hydrocarbons and other compounds containing variable amounts of sulfur, nitrogen, and oxygen, which may vary widely in volatility, specific gravity, and viscosity. Metal-containing constituents, notably those compounds that contain vanadium and nickel, usually occur in the more viscous crude oils in amounts up to several thousand parts per million and can have serious consequences during processing of these feedstocks (Speight, 1982).

There are three main classes of hydrocarbons. These are based on the type of carbon–carbon bonds present. These classes are (Fahim *et al.*, 2010):

2.1 Saturated hydrocarbons contain only carbon–carbon single bonds. They are known as paraffins (or alkanes) if they are acyclic, or naphthenes (or cycloalkanes) if they are cyclic.

2.2 Unsaturated hydrocarbons contain carbon–carbon multiple bonds (double, triple or both). These are unsaturated because they contain fewer hydrogens per carbon than paraffins. Unsaturated hydrocarbons are known as olefins. Those that contain a carbon–carbon double bond are called alkenes, while those with carbon–carbon triple bond are alkyenes.

2.3 Aromatic hydrocarbons are special class of cyclic compounds related in structure to benzene.

It is generally recognized that crude oils are composed of four major fractions which are saturates, aromatics, resins, and asphaltenes (SARA) that differ from one another sufficiently in solubility and adsorptive character that the separation can be achieved by application of relevant methods. The figure below shows an example of the SARA separation scheme which depends on the solubility of crude oil (Speight, 1992).

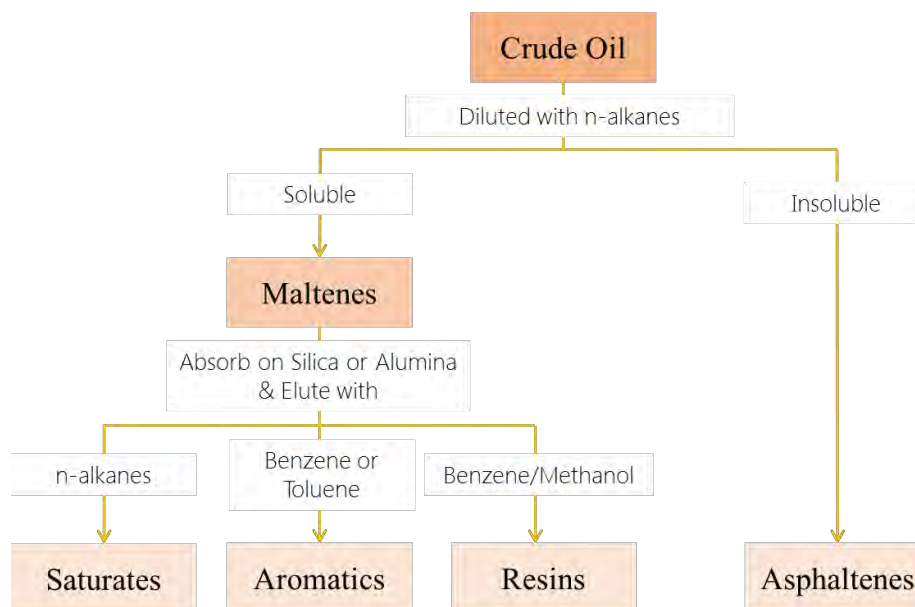


Figure 2.1 SARA separation schematics (Speight, 1992).

However, there is no one parameter that is operational in the separation of asphaltenes; the relevant parameters for asphaltene separation are physical and chemical in nature and include: temperature, pressure, polarity, aromaticity, molecular weight (molecular size), structure (the micelle), solvent, time required to precipitate/extract liquid to penetrate the micelle, ratio of the precipitating/extracting liquid to crude oil (Speight, 1992).

2.2 Asphaltene

2.2.1 Asphaltene Definition and Composition

Asphaltenes are dark brown friable solids that have no definite melting point and usually leave carbonaceous residue on heating. They are made up of condensed polynuclear aromatic layers linked by saturated links. These layers are folded, creating a solid structure known as a micelle. Their molecular weights span a wide range, from a few hundred to several million. Asphaltenes are separated from petroleum in the laboratory using non-polar solvents such as pentane and n-heptane.

Liquefied petroleum fractions (propane and butane) are used commercially in deasphalting residues and lube stock oils. (Fahim *et al.*, 2010)

The presence of high amounts of asphaltenes in crude oil can create tremendous problems in production because they tend to precipitate inside the pores of rock formations, well heads and surface processing equipments. They may also lead to transportation problems because they contribute to gravity and viscosity increases of crude oils. In refinery operations, asphaltenes have markedly adverse effects on the processability of crude oils. They lead to coke formation and metal deposition on the catalyst surface causing catalyst deactivation (Fahim *et al.*, 2010).

Asphaltenes are not a pure component and it contains a number of species which have similar solubility behavior but may have different chemical structures, sizes, and shapes. Nonetheless, asphaltene species share some common features; they are polynuclear aromatics that also contain n-alkane chains, cyclic alkanes, and heteroatoms such as sulphur, nitrogen and oxygen, as well as traces of heavy metals like nickel, vanadium and iron (Tharanivasan, 2012). In Figure 2.2, the hypothetical structures for asphaltenes of different origins, and Figure 2.3 shown in 3D structure of the asphaltene molecule from the Athabasca sand oil.

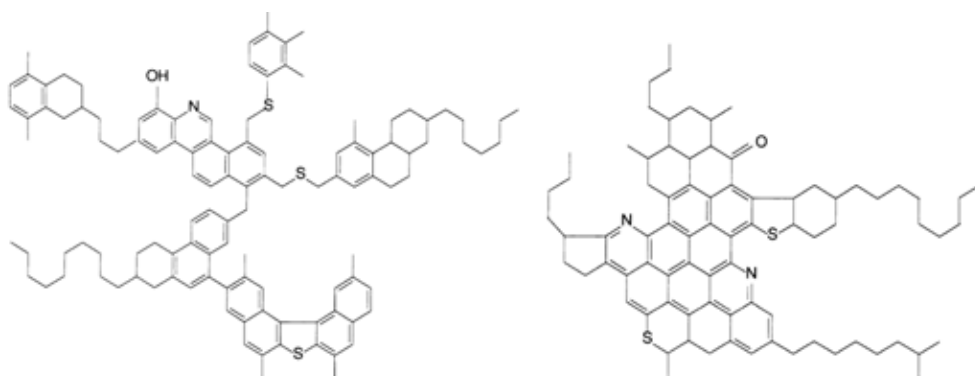


Figure 2.2 The hypothetical structures for asphaltenes of different origins (from Sheu and Mullins, 1995).



Figure 2.3 3D structure of the asphaltene molecule from the Athabasca sand oil (Murgich *et al.*, 1999).

It is found that Speight (1999) has provided the elemental composition of asphaltenes extracted from various crude oils around the world (shown in Table 2.1). A typical asphaltene molecule may contain sulphur as thiophenes, thiols, sulphides, disulphides and oxidized forms. Nitrogen can exist as pyrroles and pyridines structures. Oxygen has been identified in carboxylic, phenolic and ketonic locations, and metals (nickel and vanadium) are present as porphyrins.

Asphaltenes are generally claimed to be the “highly polar” fraction in the crude oil. This statement is based on the fact that asphaltenes are insoluble in n-heptane, a non-polar solvent. The asphaltenes are, however, easily soluble in relatively non-polar solvents like benzene, toluene and dichloromethane, whereas they are insoluble in polar solvents like water, glycerine and methanol. Hence, asphaltenes are non-polar chemically and relatively more polar when compared to other components of crude oil (Tharanivasan, 2012).

Table 2.1 Asphaltene composition from worldwide sources (Tharanivasan, 2012)

	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	0.6 - 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

2.2.2 Separation of Asphaltenes

To separate asphaltenes from crude oils, there are many methods to perform. One of them is solvent treatment (or precipitation method) which separates according to its solubility nature of asphaltenes. It is also considered to be a common approach which does not require advanced technology and; therefore, widely used. If solvent is chosen carefully, it would result in an effective separation between the constituents of conventional petroleum, heavy oil, residua, and tar sand bitumen according to differences in molecular weight and aromatic character.

In addition, the nature and the quantity of the components separated are another factor to be controlled which depends on the conditions of the experiment such as the degree of dilution temperature and the nature of the solvent. On the basis of the solubility in a variety of solvents, asphaltene are categorized into (1) carboids - insoluble in carbon disulfide, (2) carbenes - soluble in carbonic disulfide but insoluble in carbon tetrachloride; (3) asphaltenes - soluble in carbon disulfide and carbon tetrachloride, but insoluble in the low-boiling saturated hydrocarbons, such as petroleum ether; and (4) malthenes - soluble in low-boiling saturated hydrocarbons (maltenes include resins and oils) (Yen and Chilingarian, 1994). The solubility of asphaltene in different solvents is shown in Table 2.2.

Table 2.2 Solubility of asphaltenes in various solvents (Mitchell *et al.*, 1972)

Solvent	$\delta = \gamma_{\zeta}^{-1/3}$	Solubility (%wt)
<i>Normal hydrocarbons</i>		
Pentane	3.2	0.0
Hexane	3.5	18.9
Heptane	3.8	30.1
Octane	3.9	28.9
Nonane	4.0	40.3
Decane	4.1	43.2
<i>Olefins</i>		
Pentene	3.4	2.8
Hexene	3.6	21.3
Heptene	3.8	32.9
Octene	4.0	43.9
Nonene	4.0	47.2
Decene	4.1	47.7
<i>Ethers</i>		
Ethyl ether	3.5	15.3
n-Propyl ether	3.8	22.9
n-Butyl ether	4.0	30.0
n-Amyl ether	4.2	36.5
Ethyl-1-butyl ether	3.5	19.5
<i>Ketones</i>		
Acetone	5.3	4.1
3-Pentanone	5.2	17.8
Acetophenone	7.8	100.0
2-Pentanone	5.1	27.0
Methylethyl ketone	5.4	18.2
Methylisobutyl ketone	4.7	11.5
<i>Alcohols</i>		
n-amyl alcohol	5.2	3.3
Ethylene glycol	12.2	4.2

Asphaltenes and maltenes are two general fractions obtained from separating crude oils. The light molecular weight of hydrocarbons tends to suspend in the fluid phase. The higher molecular weight and complicated structure of hydrocarbon derivatives, on the other hands, would precipitate especially well by volumes of n-pentane or n-heptane in the methods generally preferred at present,

although hexane is used occasionally. In Figure 2.4, the graph shows the amount of asphaltene yield according to number of carbon used as precipitant solvent (Speight, 1982). There are also other standard method to separate asphaltene from crude oils (deasphalting) shown in Table 2.3.

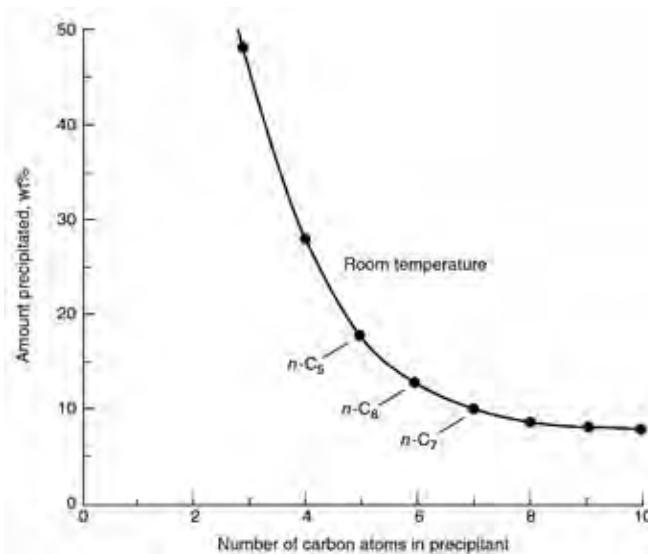


Figure 2.4 Asphaltene yielded with a number of carbon in precipitant (Speight, 1982).

Table 2.3 Standard method of asphaltene precipitation (Speight, (1982))

Methods	Precipitant	Volume per gram of precipitant
ASTM D893	n-pentane	10 mL
ASTM D2006	n-pentane	50 mL
ASTM D2007	n-pentane	10 mL
ASTM D3279	n-heptane	100 mL
ASTM D4124	n-heptane	100 mL
IP 143	n-heptane	30 mL

2.2.3 Asphaltene Colloidal State and Self-Aggregation

In crude oil, asphaltene are present as discrete or colloiddally dispersed particles in the oily phase. As the various low boiling and intermediate petroleum oils are removed during the distilling process, the particles of asphaltene are massed together to form larger particles. It is believed that asphaltene exists in an oil-external (Winsor's terminology) or reversed micelle. The polar groups are oriented towards the center, which can be water, silica (or clay), or metals (V, Ni, Fe, etc.). The driving force of the polar groups assembled toward the center originates from hydrogen-bonding charge transfer.(Mullins and Sheu, 1999)

Asphalts or bitumen can be treated as a colloidal system. Micellar structures are predominant in asphalts with high asphaltene content. Structural orders of asphaltenes would explain various properties existing in heavy crude and tar sand bitumens. The sizes of asphaltene increase due to association and aggregation are as follows (nm) (Mullins and Sheu, 1999):

Unit Sheet → Stacks → Aggregates → Assemblages → Clusters → Flocculation
 (1.2-2.0) (3.0) (5.0) (10.0-15.0) (200-2000) (1x10³to 20x10³)

Asphaltenes are believed to exist in solution as semicrystalline aggregates, commonly called “nanoaggregates” that exhibit stacking of large aromatic cores, surrounded by peripheral alkyl chains. X-ray diffraction measurements first identified the semicrystalline structure of asphaltenes by the presence of a broad diffraction peak corresponding to a separation distance of roughly 3.6 Å.¹⁰ This broad peak is interpreted as the stacking of the large aromatic asphaltene molecular cores and is the foundation for the “coin stack” structure of asphaltene nanoaggregates. (Hoepfner *et al.*, 2013).

The mechanism of asphaltene aggregation studied by Porte *et al.* suggests that they proceeds from specific strong interaction sites located at the periphery of the asphaltene molecules: they drive the reversible association in two-dimensional sheets, a morphology which is consistent with reported scattering and viscosity data. Precipitation eventually occurs, determined by van der Waals attractions between aggregates, when the solubility parameter of the solvent is shifted. The figure below shows the asphaltene aggregation process as molecular

weight of asphaltenes change proposed by Yen (1982). Figure 2.5 explain the progress of asphaltene aggregation.

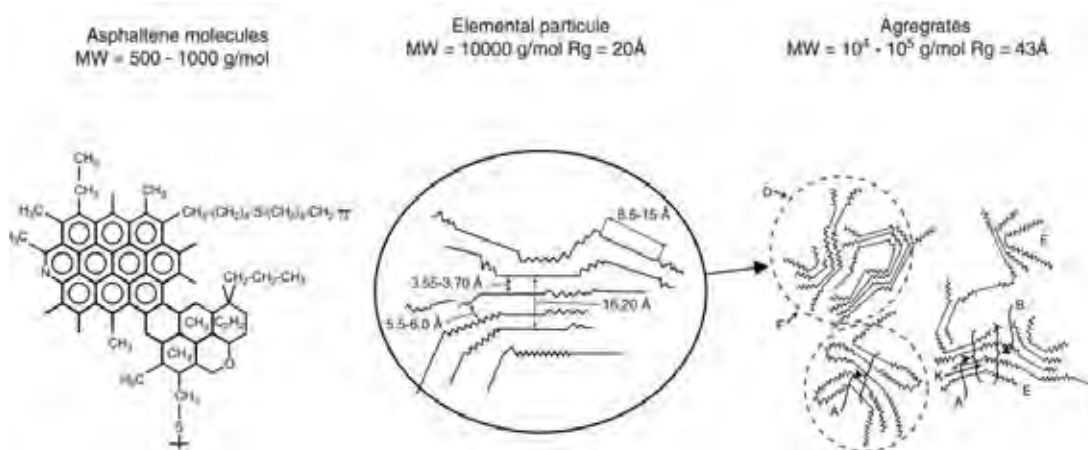


Figure 2.5 The process of asphaltene aggregation according to molecular weight (Merdrignac *et al.*, 2007).

From the study of Merdrignac and Espinat (2007), they have investigated the characteristics of asphaltene colloidal state from different techniques such as vapor pressure osmometry (VPO), size exclusion chromatography (SEC), mass spectrometry, Small Angle X-ray and Neutron Scattering (SAXS and SANS) and the NMR. One of their discoveries is that an increase of the temperature induces a dissociation of the aggregates which leads to a decrease of the molecular weight. In the same way, molecular masses tend to decrease with the dissociating solvent power. In addition, in such apolar solvents, asphaltenes tend to strongly associate and the presence of aggregates is detected whatever the concentration. In Figure 2.6, the graphs illustrate the influences of temperature and the different solvents on asphaltene aggregation.

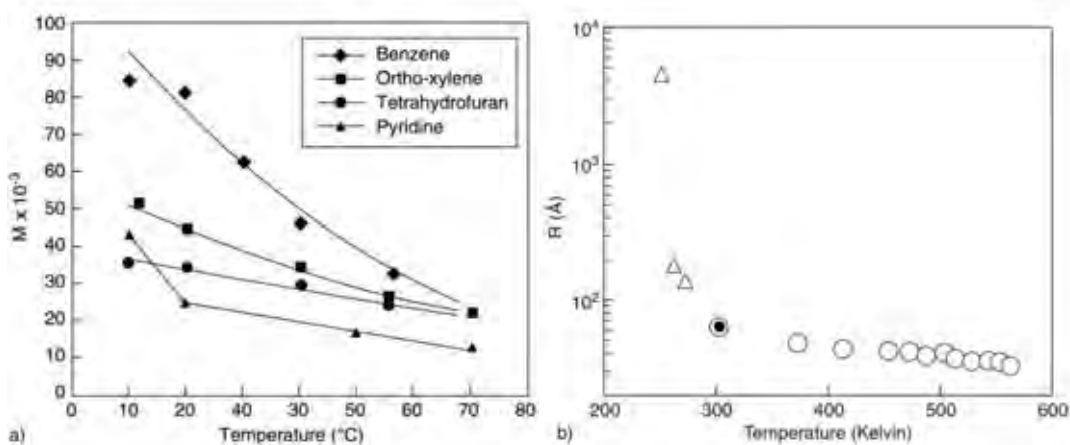


Figure 2.6 Temperature and solvent effects on asphaltene aggregation: a) average molecular weight M_w of Safanyia vacuum residue asphaltenes in solution in different solvents (● tetrahydrofuran, ■ ortho-xylene, ◆ benzene, ▲ pyridine); b) radii of gyration versus temperature (Merdrignac *et al.*, 2007).

To understand the asphaltene aggregation, there are terms to be described, one of them is destabilization which refers to both the phase separation or increase in aggregation tendency of nanoparticles and the subsequent collision and eventual aggregation of asphaltene nanoparticles into aggregates. Destabilization is usually induced by adding a precipitant rather than changing the temperature or pressure. Detection techniques, such as optical microscopy, light scattering, ultraviolet–visible (UV–vis) spectrophotometry, and refractive index, have been used to detect the precipitated micrometer-sized particles for different precipitants and precipitant concentrations.

Many studies assume that destabilized nanosized asphaltene aggregates instantaneously grow into sizes detectable via conventional techniques. Such an assumption is only valid for the experimental conditions that produce strong attractive forces between aggregating asphaltenes and where the only rate-limiting step is the diffusion of asphaltene particles. However, at low precipitant concentrations, weaker attractions between asphaltene particles could lead to a reaction-limited process, where slow kinetics become significant. (Haji-Akbari *et al.*, 2013)

Maqbool *et al.* (2011) showed that the time that it takes to detect asphaltene instability at low precipitant concentrations can be on the order of weeks or even months. Even in the case of higher precipitant concentrations, where instabilities can be detected immediately, it can still take up to several weeks for the measured solubility of asphaltenes to reach its final value. Therefore, the existing thermodynamic models that are developed on the basis of the assumption that the conducted experiments attained immediate solubility equilibration can lead to misleading predictions about the asphaltene behavior under different conditions.

Another study from Hoepfner *et al.*, they found that asphaltenes are believed to exist in solution as semicrystalline aggregates, commonly called “nanoaggregates”, that exhibit stacking of large aromatic cores, surrounded by peripheral alkyl chains. Aggregation proceeds from specific, strong interaction sites located at the periphery of the asphaltene molecules that drives the reversible association in two-dimensional sheets, a morphology that is consistent with reported scattering and viscosity data.

2.2.4 Solubility of Asphaltene

From Hansen (2000), solubility parameters are sometimes called cohesion energy parameters as they are derived from the energy required to convert a liquid to a gas. The energy of vaporization is a direct measure of the total (cohesive) energy holding the liquid’s molecules together. All types of bonds holding the liquid together are broken by evaporation, and this has led to the concepts described in more detail later. The term cohesion energy parameter is more appropriately used when referring to surface phenomena.

The term solubility parameter was first used by Hildebrand and Scott. The earlier work of Scatchard and others was contributory to this development. The Hildebrand solubility parameter is defined as the square root of the cohesive energy density:

$$\delta = (E/V)^{1/2} \quad (1)$$

$$\delta = \sqrt{C} = \left[\frac{\Delta H - RT}{V} \right]^{1/2} \quad (2)$$

Where δ is solubility parameter ($\text{MP}^{1/2}$), V = molar volume of the pure solvent, E is its energy of vaporization, C is cohesive energy density, V is molar volume, ΔH is heat of vaporization, R is gas constant and T is temperature.

After the Hildebrand solubility parameter, there was many researchers attempted to improve the definition and the mathematical formula presented in Hildebrand book. One of them was Burrell and others (Burrell et al. 1968) which has related solubility parameter particularly with coatings and adhesion phenomena.

However, Hansen (2000) has proposed another theory of solubility parameter called Hansen solubility parameters (HSPs). The fundamentals of the HSPs are that the total energy of vaporization of a liquid consists of several individual parts. These arise from (atomic) dispersion forces, (molecular) permanent dipole–permanent dipole forces, and (molecular) hydrogen bonding (electron exchange).

Any chemicals with similar HSP values have high affinity for each other. The extent of the similarity in a given situation determines the extent of the interaction. For example, Ethanol and nitromethane (26.1 and 25.1 $\text{MP}^{1/2}$ respectively), the values are closed but the polarity and affinities between these two are also need to be considered. With different properties, there are possibilities that, two chemicals might not be completely mixed in one another.

There are three major types of interactions in common organic materials. The most general are the nonpolar interactions. As molecules are built up from atoms, all molecules contain those types of attractive forces. For the saturated aliphatic hydrocarbons, for example, these are essentially the only cohesive interactions, and the energy of vaporization is assumed to be the same as the dispersion cohesive energy, E_D .

Another type of interactions is the polar cohesive energy, E_P , which is caused by the permanent dipole–permanent dipole interactions. These are inherently molecular interactions and are found in most molecules to one extent or another. As noted previously, the most polar of the solvents include those with relatively high total solubility parameters that are not particularly water soluble.

The third major cohesive energy source is hydrogen bonding, E_H . This can be called more generally an electron exchange parameter. Hydrogen bonding is a molecular interaction and resembles the polar interactions in this respect. The basis of this type of cohesive energy is attraction among molecules because of the hydrogen bonds.

To calculate the solubility parameters (HSPs), all three molecular interaction must be taken into account. Hansen has proposed the method to calculate HSPs which came from the total cohesion energy, E , must be the sum of the individual energies that make it up.

$$E = E_D + E_P + E_H \quad (3)$$

Dividing this by the molar volume gives the square of the total (or Hildebrand) solubility parameter as the sum of the squares of the Hansen D, P, and H components.

$$E/V = E_D/V + E_P/V + E_H/V \quad (4)$$

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (5)$$

A study of asphaltene from Hsienjen *et al.* (1993), they found that different compositions in asphalts have a different miscibility in solvents because different fractions exhibit different miscibilities in solvents, and the miscibilities of different asphaltenes in solvents are slightly different because different compositions of asphaltenes are not dissolved to the same degree in solvents.

Buckley and Wang (2002) estimated solubility parameter from refractive index (RI). They found that nonpolar molecules had a solubility parameter linearly related to RI as shown in Figure 2.7. The function of RI, F_{RI} , is defined by the following equation, where F_{RI} is refractive index function, n is the refractive index, and δ is solubility parameter.

$$F_{RI} = \frac{(n^2 - 1)}{(n^2 + 2)} \quad (6)$$

$$\delta = (52.042 * F_{RI}) + 2.904 \quad (7)$$

With measurement of refractive index, solubility parameters can be estimated which will be applied in this study as well as Hansen solubility parameters theories.

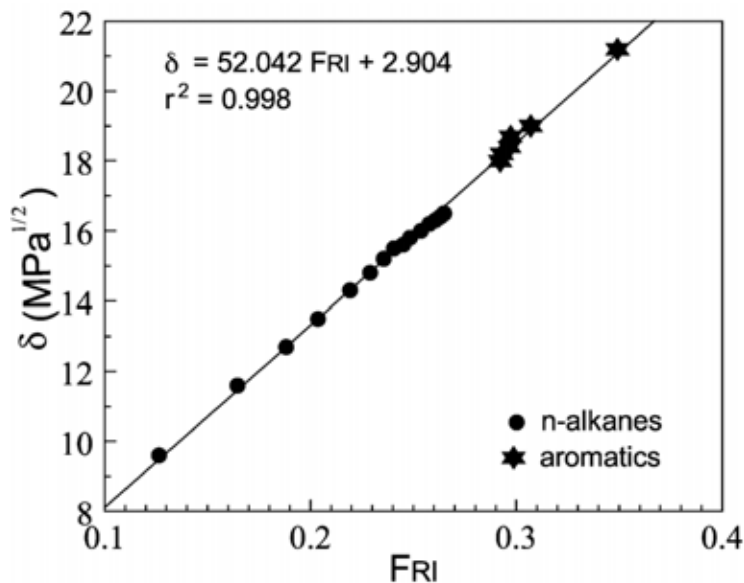


Figure 2.7 Linear relationship between solubility parameter of nonpolar molecules and refractive index (FRI) (Buckley *et al.*, 2002).

2.3 Effect of Water on Asphaltene Aggregation

There were many researches that investigated on water existence in asphaltene. One of them is from Murgich *et al.* (2002), which studied the molecular mechanisms of water in asphaltene aggregation. They found that the average model asphaltenes which have saturated rings and rather short alkane chains attaches to their aromatic cores. Some of the chains act as bridges between the aromatic regions, so that the molecules have quite complex spatial conformations. In general, several heteroatoms (S, N, O) are also present in these molecules. With the existence of atomic groups containing basic N and O atoms implies not only that the asphaltene molecules will be polar but also that they may interact with molecules capable of H bonding with water.

The H bond is a strong interaction that contains contributions from all the intermolecular forces. It involves the interaction of a H atom, attached to a highly electronegative one (i.e., O, N), with an electronically rich atom of a neighboring molecule or molecular fragment. This type of interaction between fragments and molecules with closed electronic shells is mostly determined by the local atomic

charges of both of them (electrostatic interaction). Little or no charge transfer in the H bond is found, although noticeable charge rearrangements may occur in both molecules, through polarization and induction effects.

H bonding may contribute to the aggregate generation through its formation in different sites of the asphaltene molecules. These sites must be free of steric hindrances in such a way that proper interatomic contact is possible between the approaching water (or other acidic) molecule and the accepting groups. Moreover, the strength of H bonding is orientation dependent, so the approach of the molecules involved should be at proper angles to generate a strong interaction. Otherwise, the H bond will be weak and contribute little to the aggregation process. As the asphaltene molecules may contain several kinds of basic sites, it is expected that H bonding will contribute to the aggregate formation if they are available for interaction.

In conclusion of the Murgich *et al.* (2002) discoveries, the forces acting in the aggregates of organic molecules contain contributions from: a) the intermolecular charge transfer, b) the electrostatic (Coulombic) interaction between the molecular charges, c) the always present van der Waals interaction, d) the short range exchange repulsion energy, and e) a weak one from the induction. The interactions between the asphaltene and resin molecules as well with the rest of the crude contain contribution from all these forces. In most cases, the combination of the van der Waals, Coulombic and repulsive exchange interactions are the main forces acting in these aggregates. In a few words: there is no mystery involved in the forces holding together the molecular aggregates of asphaltenes and resins.

Another important study from Langevin *et al.* (2004) provided basic understanding of how water emulsion becomes a factor determining asphaltene aggregation. It was found that crude oils, especially the heavy oils, contain large quantities of asphaltenes (surface active components) that act as natural emulsifiers. Resins, fatty acids such as naphthenic acids, porphyrins, wax crystals, etc. cannot alone produce stable emulsions, although they are also surface active. However, they can associate to asphaltenes and affect emulsion stability.

The next question is how emulsion stability related to asphaltene aggregation. To answer this question, basic understanding of emulsion must be done. When forming emulsion, the emulsifier (asphaltene) forms a thin layer (film)

surround the hydrophilic/hydrophobic part and become emulsion. Surfactant adsorption is generally very fast, but for larger molecules, such as asphaltenes, the adsorption process is longer and adsorption is generally irreversible. In certain circumstances, asphaltenes can adsorb in the form of aggregates, the surface layers become thick, and a solid-like “skin” is formed.

The emulsions formed by asphaltene are rather stable. It is because when asphaltenes form “skins” at the oil-water interface, thinning of emulsion films (film rupture) is very complex: films are thick and irregular, large aggregates are trapped in the film and stop the thinning process. In other words, asphaltene aggregate would stick to the oil-water interface and remains stable on the interface instead of from large particles between asphaltene.

2.3.1 Fraction of Asphaltene Based on Asphaltene Adsorption on the Oil-Water Interface

One of the major problems encountered in crude oil or heavy oil production is the formation of stable W/O emulsions. Resolution of these emulsions and water removal from oil feed to upgrading facilities are important steps in the petroleum industry. A great deal of research has been focused on understanding the stabilization mechanisms of W/O emulsions. However, as mentioned in Qiao *et al.* (2016) articles which stated that only a small fraction of asphaltenes is responsible for W/O emulsion stabilization, this fraction is called interfacially active asphaltene (IAA), or in other words, the asphaltene that can form emulsion with water is IAA.

According to Qiao *et al.* (2016) study, they developed the method that can separate IAA out from the whole asphaltene by adding water and then extracted IAA, the procedure illustrated in Figure 2.8. By this mean, the IAA is obtained and then examined. From the result of the investigation, they concluded that the stabilization of W/O emulsions by asphaltenes was found mainly as a result of the IAA subfraction, which is accounted for less than 2% of whole asphaltene.

Another interesting point is that the high interfacial activity of IAA molecules and their ability to produce rigid films with aging was linked to their high content of sulfoxide groups, which could induce the hydrogen-bonding interactions between IAA molecules and water as well as neighboring IAA molecules.

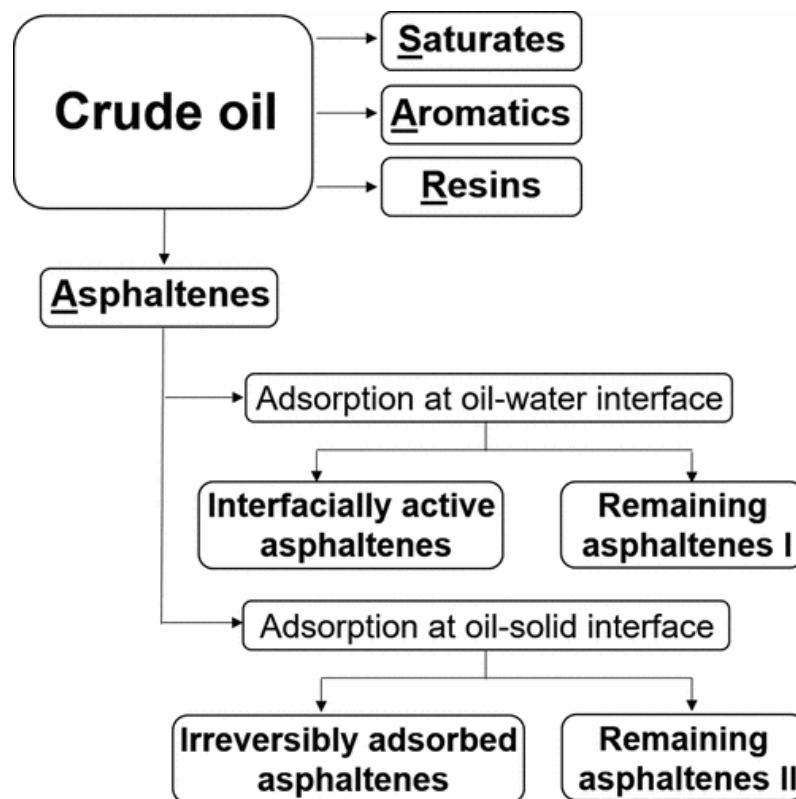


Figure 2.8 Extended-SARA (E-SARA), a concept of asphaltene fractionation according to their interfacial activities and adsorption characteristics (Qiao *et al.*, 2016).

2.4 Asphaltene Aggregation Model

From Haji-Akbari *et al.* (2013), they provided the mathematic method to estimate the aggregation rates by accounting for the properties governing the aggregation kinetics using Smoluchowski's aggregation model.

According to Maqbool *et al.* (2011), the rate of asphaltene aggregation is controlled by two important factors:

- 1) frequency of collision between aggregating particles
- 2) fraction of successful collisions that lead to aggregation

The rate of formation of each particle in Smoluchowski's model is given by

$$\frac{dy}{dx} = \frac{1}{2} \sum_{i+j=k} K_{ij} C_i C_j - C_k \sum_{i \geq 1} K_{ik} C_i \quad (8)$$

Where
$$K_{ij} = \frac{8k_B T}{3\mu} = K \quad (9)$$

C_i = concentration of particles of size i (number of particles/m³)

K_{ij} = collision kernel for aggregation (m³/s)

k_B = Boltzmann constant (m² kg s⁻² K⁻¹)

During the reaction-limited aggregation, only a fraction of Brownian collisions can lead to the Formation of larger particles. To account for unsuccessful collisions, the rate constant will be given by

$$K = \frac{8k_B T}{3\mu} \beta \quad (10)$$

Where β = collision efficiency = $\frac{\text{number of successful collisions}}{\text{total number of collisions}}$

Using the exponential Ansatz procedure, equation 8 becomes

$$\frac{C_k(t)}{C_1(0)} = \frac{4}{(at + 2)^2} \left[\frac{at}{at + 2} \right]^{k-1} \quad (11)$$

Where

$$\alpha = \frac{8k_B T}{3\mu} \beta C_1(0)$$

$C_1(0)$ = The initial concentration of aggregating asphaltenes at time zero

From Equation 11, detection time can be estimated from the following parameters

- 1) Viscosity
- 2) Collision Efficiency
- 3) Initial concentration of asphaltene nanoparticles

As a result, $t_{\text{detection}}$ followed the equation given below

$$t_{\text{detect}} \propto \frac{1}{\sqrt{C_1(0)}} \frac{\mu}{\beta} \quad (12)$$

To determine β , or collision efficiency, Fuch's stability ratio (W) between colliding particles of equal size is used to estimate the collision efficiency from the interparticle potential $U(t)$.

$$\frac{1}{\beta} = W = 2r_0 \int_{2r_0}^{\infty} \frac{\exp\left(\frac{U_t(s)}{k_B T}\right)}{S^2} ds \quad (13)$$

Where

r_0 - the radius of primary particles (m)

U_t - the total energy of interaction between two primary particles (J)

S - the distance between the centers of the particles (m)

k_B - Boltzman's constant ($m^2 \text{ kg s}^{-2} \text{ K}^{-1}$)

T - is the temperature (K)

The major contribution to the stability ratio is from the separation distances close to U_{max} ; therefore, the collision efficiency defined in Equation 13 can be estimated using the following correlation;

$$\beta = \exp\left(-\frac{U_{max}}{k_B T}\right) \quad (14)$$

To obtain U_{max} , Flory–Huggins theory of polymer–solution thermodynamics is used to correlate the solubility parameters of the solute and solvent with the U_{max} given in the equation below;

$$U_{max} \propto \frac{1}{(\delta_{asp} - \delta_{solution})^2} \quad (15)$$

Where

δ_{asp} = Hildebrand solubility parameter ($\text{Pa}^{0.5}$) of the asphaltenes

$\delta_{solution}$ =Hildebrand solubility parameter ($\text{Pa}^{0.5}$) of the solution

Combine equation 14 and 15 to obtain

$$-\ln(\beta) \propto \frac{1}{(\delta_{asp} - \delta_{solution})^2} \quad (16)$$

From equation 12, take \ln both sides

$$\ln\left(\frac{t_{detect} \sqrt{C_1(0)}}{\mu}\right) \propto -\ln(\beta)$$

Then combine the current equation with equation 16

$$\ln\left(\frac{t_{\text{detection}}\sqrt{C_1(0)}}{\mu}\right) \propto \frac{1}{(\delta_{\text{asph}} - \delta_{\text{solution}})^2}$$

CHAPTER III

EXPERIMENTAL

3.1 Equipment

3.1.1 Optical microscope from Nikon (Eclipse E600 model) with 50× objective lens and 10× eyepiece

3.1.2 Branson 5510 sonicator

3.1.3 Qsonica Q700 sonicators with standard ½” probe

3.1.4 Magnetic stirrer from IKA® MINI MR Standard

3.1.5 Magnetic stirrer from IKA® RO10 WERKE

3.1.6 Masterflex L/S Tubing Pumps, model EW-07522-20

3.1.7 Sorvall Legend X1R and Eppendorf 541R centrifugation equipment

3.2 Chemicals

3.2.1 Alice (Tabish) pretreated crude oil

3.2.2 n-Heptane (HPLC Grade, 96% min by GC)

3.2.3 Deionized water

3.3 Methodology

3.3.1 Asphaltene Separation from Crude Oil

3.3.1.1 Homogenize crude oil by stirring it at moderate temperature and continue for at least 30 minutes. Then have homogenized crude oil centrifuged at 40,000 rpm for 3 hours to remove contaminants such as sand, water, wax, and soils from the crude oil. Knowing that the crude oil obtained from this step would be used to study the asphaltene aggregation behavior.

3.3.1.2 Separate the supernatant out and mix with n-pentane (ratio of pentane to crude oil is 40:1). After that, centrifuge for another half an hour to let asphaltene precipitate and stabilize at the bottom. The cake obtained from the

centrifugation is asphaltene which needs to have pentane evaporated before utilizing it.

3.3.1.3 For the supernatant, use rotary evaporator to dry off pentane in order to acquire maltene.

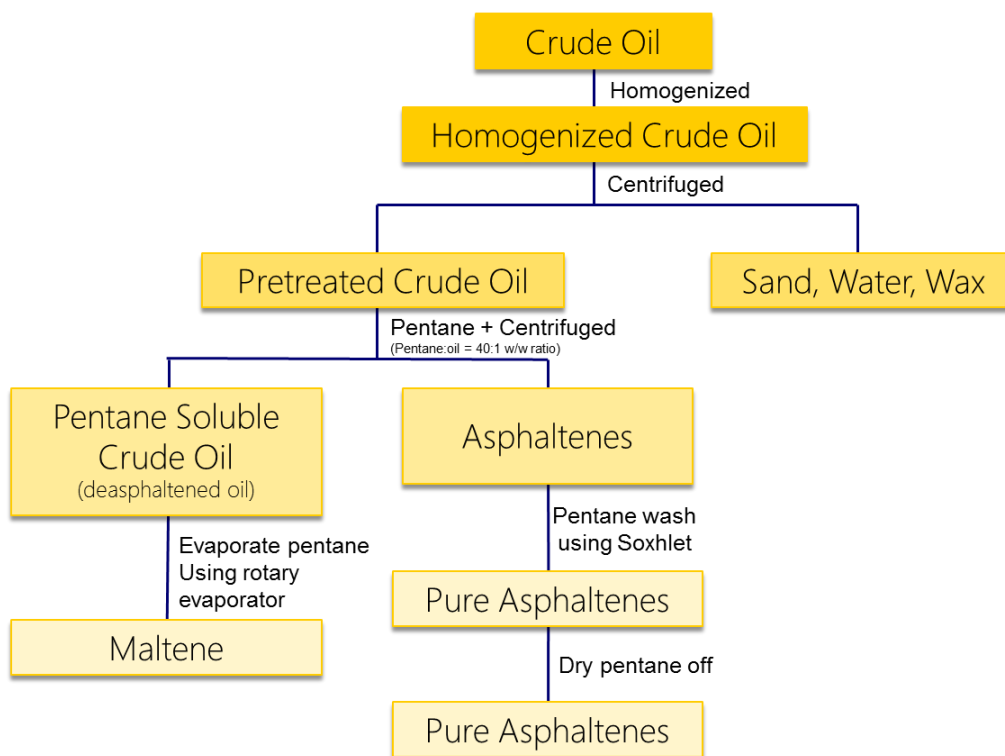


Figure 3.1 Schematic of asphaltene separation.

3.3.2 Model Oil Preparation

3.3.2.1 A known concentration of crude oil and water is added to a 25 mL flask in order to perform an experiment.

3.3.2.2 The flask will be tilted to the right or left which makes the liquid stay in the particular area as illustrated in Figure 5.2. After obtaining a right position, the homogenization can be started.

3.3.2.3 The time for homogenization can be varied in accordance with the amount of mixture and the size of the emulsion. Typically, the homogenization is conducted for 10 minutes.

3.3.2.4 During homogenizing process, the flask should be revolved around the tip so that the entire mixture is touched by the tip.

3.3.2.5 After the homogenization is completed, the cleaning can be done by using delicate wipers with chloroform and have the tip dipped in the flask containing chloroform.

3.3.2.6 Confirm the homogenization of solution by optical microscope (Nikon).

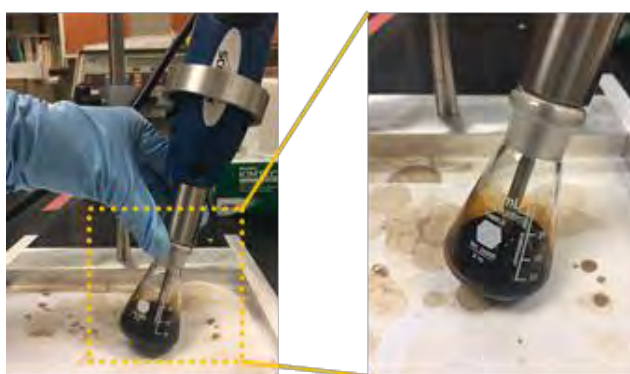


Figure 3.2 The position of homogenization with 25 mL flask.

3.3.3 Detection Time Experiment

3.3.3.1 Place known amount (usually 0.3-0.9 g) of model oil in a 25 mL flask and cover with stopper to prevent evaporation.

3.3.3.2 Induce asphaltene precipitation by adding the precipitant, which in this case is n-heptane. Add n-heptane slowly to the model oil using Masterflex L/S Tubing Pumps (Figure 5.3) at a rate of (approximately) 0.5 mL/min. During the heptane addition, all mixtures will be kept well-mixed using magnetic stirrers (Magnetic stirrer from IKA® MINI MR Standard) to minimize localized high heptane concentrations which could lead to significant error.



Figure 3.3 Masterflex L/S Tubing Pumps, model EW-07522-20.

3.3.3.3 After heptane addition, take a droplet of well-stirred mixture using pipette tip connected to a plastic pipet and place under the microscope at different time to detect asphaltene particles. The time to collect samples was set in a certain period of time shown in table 5.1. The picture of samples at different time will be captured by the microscope and recorded in a computer which was later arranged in order. Keep taking the sample droplet until the precipitation is completed. The resolution of the microscope used in this research is high enough to detect particle at approximately $0.5 \mu\text{m}$ in diameter. The average of earliest time when haze and particles are observed is defined as the detection time.

3.3.3.4 After the precipitation completed, arrange the recorded photo in order of time and calculate the rate of precipitation of asphaltene.

3.3.3.5 Repeat the experiment with different concentration of heptane. Normally, the next concentration is 2%wt lower than the previous experiment. For example, if 70%wt heptane, has completely finished, then, the next concentration of heptane that should be carried out is 68%wt and continue lowering until there are enough points to plot the graph which approximately 5 points including short (10 hours) and long period of precipitation (up to 100 hours).

3.3.3.6 Report the results as the detection time as a function of heptane concentration. The heptane concentration reported here is the volume heptane added per volume of model oil.

Table 3.1 Time interval established for collecting samples

Elapsed Time		Sample collecting interval
Starting Time	Ending Time	
0 min	40 min	5 minutes
40 min	1 hr 40 min	10 minutes
1 hr 40 min	3 hr	20 minutes
3 hr	5 hr	40 minutes
5 hr	9 hr	1 hour
9 hr	15 hr	2 hours
15 hr	18 hr	3 hours
18 hr	1 day 6 hr	4 hours
1 day 6 hr	2 days	6 hours
2 days	2 days 10 hr	10 hours
2 days 10 hr	2 days 22 hr	12 hours
2 days 22 hr	3 days 12 hr	14 hours
3 days 12 hr	4 days 6 hr	18 hours
4 days 6 hr	5 days 4 hr	22 hours
More than 5 days 4 hr		24 hours

3.3.4 Centrifugation Experiment

3.3.4.1 Choose any specific concentrations of model oil such as 1%wt of water in crude oil. (knowing that the chosen concentrations should be efficiently high in order to provide a clear evidence of self-stabilization or self-association of asphaltene).

3.3.4.2 Have empty microcentrifuge tubes prepared and put them in an oven which temperature is set at 70° Celsius. Leave them overnight.

3.3.4.3 Have the microcentrifuge tube in Silica Gel Desiccator before using for 20 minutes and then weight empty centrifuged tubes.

3.3.4.4 Place the model oil in the tubes and weight one more time. Record the weight of the model oil before heptane addition.

3.3.4.5 Add the heptane to the model oil until it reaches desired concentration. The mixture will be sonicated using Branson 5510 sonicator to ensure homogeneity. (Depending on the purpose of the experiment, if the asphaltene content in pure crude oil is investigated, then, there is no need to add heptane in this step).

3.3.4.6 Place the sample in microcentrifuge tubes and centrifuge at 14000 rpm for 10 minutes to settle the precipitated asphaltene to the bottom. Decant the liquid from the settled asphaltenes (shown in Figure 5.4) and wash the asphaltenes several times with heptane to remove the minor quantity of crude oil adhering to the particles. Continue washing until the color of the heptane become constant (most likely yellowish). Remove the heptane out of the asphaltenes which already settled at the bottom of microcentrifuge tubes and left the sample in fume hood for 24 hours to evaporate heptane. Then, dry the asphaltenes in oven and weighed. Record the weight of asphaltenes precipitate.

3.3.4.7 Keep recording the weight of the samples until the precipitation remains unchanged which means that all of the heptane evaporated.

3.3.4.8 Report the results as the weight percentage of asphaltenes precipitate per 1 gram of model oil.

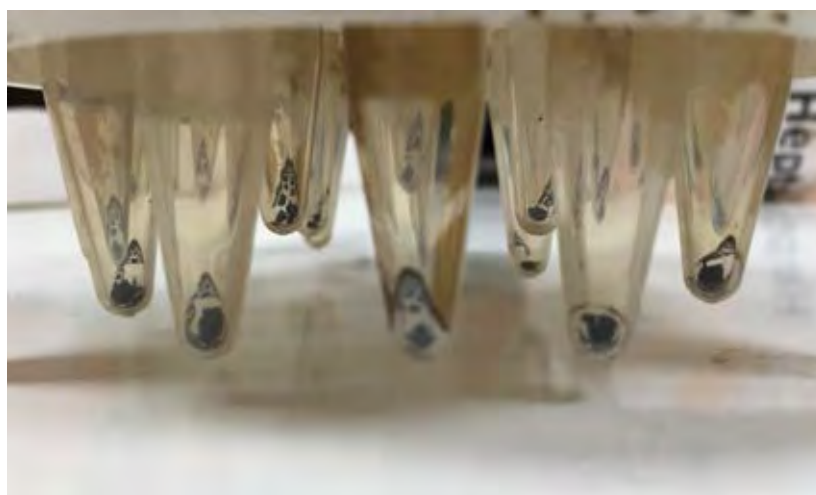


Figure 3.4 Asphaltene settled at the bottom of microcentrifuge tubes.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Detection Time Experiment (Part I) – Oil VS. Oil + Water

To study the effect of water on asphaltene aggregation, the first part is to perform detection time experiment and then plot the graph between the heptane concentration and the time detected when asphaltene nanoaggregates can be seen under the microscope (the size of asphaltene aggregates usually ≥ 0.5 microns to be detected under the microscope). This type of graph can be demonstrated as the rate of asphaltene aggregation.

To perform detection time experiment (Fig 4.1), heptane is added to oil such that its concentration in the oil-heptane mixture is lower than the concentration needed to observe aggregation immediately (~ 2 minutes). The oil-heptane mixture is then left on the stirrer to be aged. During the aging, samples are collected from the mixture and then observed under the microscope. The results from the experiment is shown in Table 4.1

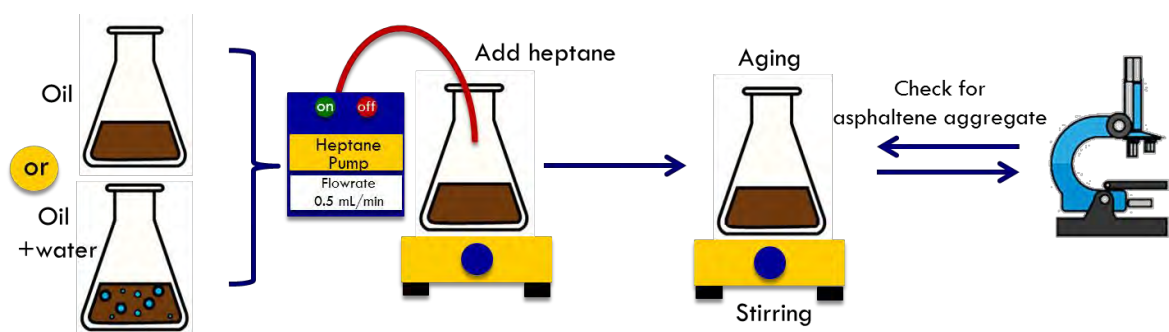


Figure 4.1 Detection time experiment for both with and without water presence.

In this first part, the experiment is carried out to compare 3 different water contents: 0 (pure oil), 0.5, 1, 5 and 10wt% water concentration as described in Figure 4.2.

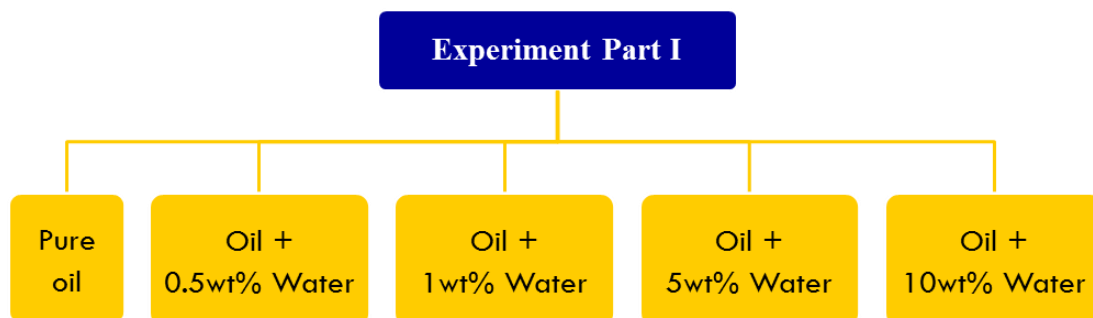


Figure 4.2 Experimental scheme part I.

Table 4.1 The pictures taken from microscope at different time compared between pure oil and oil+water. The asphaltene aggregation is those dark grey particles that stay in the bulk fluid.

Oil	Aging Time				
	30 min	1 hr	4 hr	18 hr	24 hr
Pure oil					
Oil + 1wt% Water					
Oil + 10wt% Water					

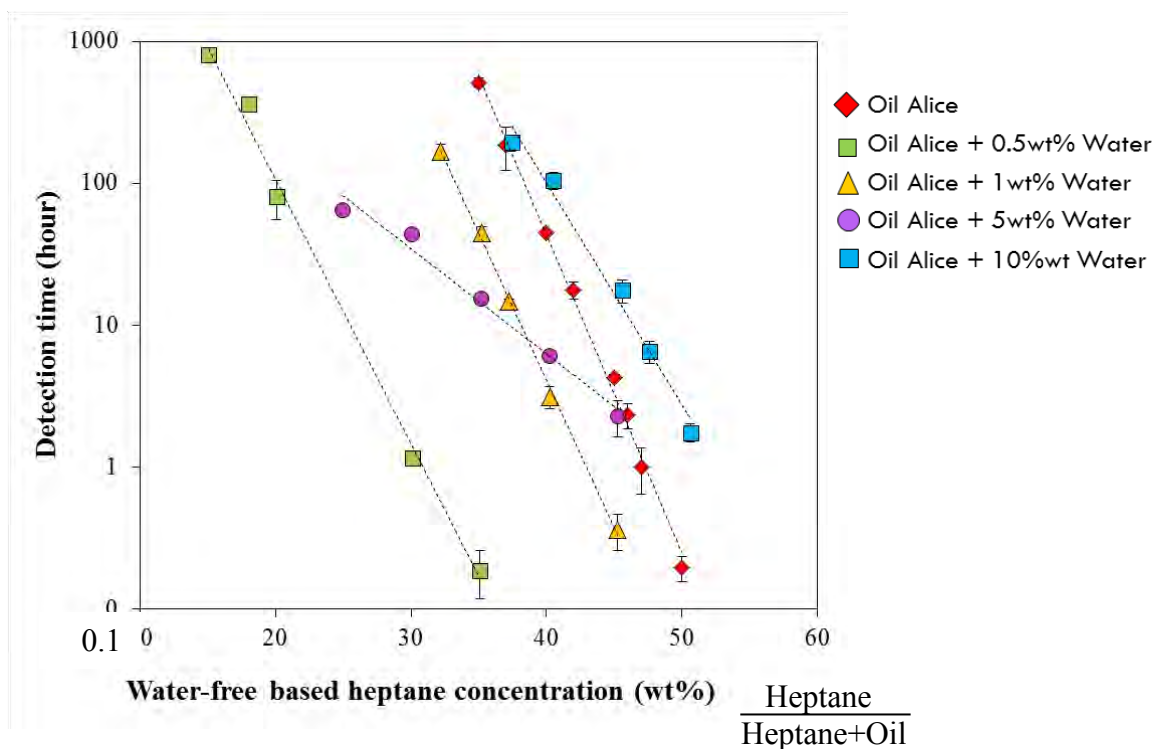


Figure 4.3 Detection time curve comparing between pure crude oil, 0.5, 1, 5 and 10wt% water in oil.

As it can be seen from the graph between time and heptane concentration (Figure 4.3), (wt%), with presence of water, there are changes to the original curve (pure oil). For the case of oil+0.5, 1 and 5 wt% water, the curve shifts to the left which means that the rate of asphaltene aggregation increases while oil+10wt%water shifts to the right, in other words, the 10wt%water mixture slows down the rate of asphaltene aggregation.

To make a clear statement, the rate of asphaltene aggregation is enhanced (the detection time curve shifted to the right) when water concentration was low (<10wt%). On the contrary, the rate decreases if the water concentration was higher than 10wt% ($\geq 10\text{wt}\%$). There are two controversial trends when water content is different. In Figure 4.4, the graph between water content and detection time is plotted in order to illustrate 2 different trends. One is increasing and another one is decreasing the rate of asphaltene aggregation.

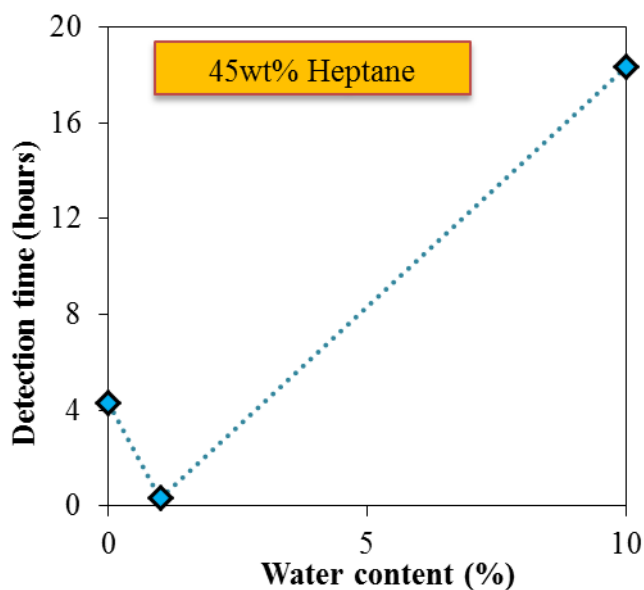


Figure 4.4 The water content is plotted against detection time, 2 controversial trends are shown (at the 45wt% heptane concentration).

However, a problem was raised due to the fact there might be a possibility of misreading the detection time in the presence of water. From visual aspect, it is difficult to tell three phases apart from one another in case of water presence, as illustrated in Figure 4.5. Having emulsified water in the system makes it uncertain for determining the exact time of asphaltene aggregation. Consequently, the reading is inaccurate and leads to arguing statement. From this detection time curve, the only observation that can be made is water play an important role in asphaltene aggregation.

In the next part of the experiment, the procedure is implemented from the first part which water is removed from the system by centrifugation method.

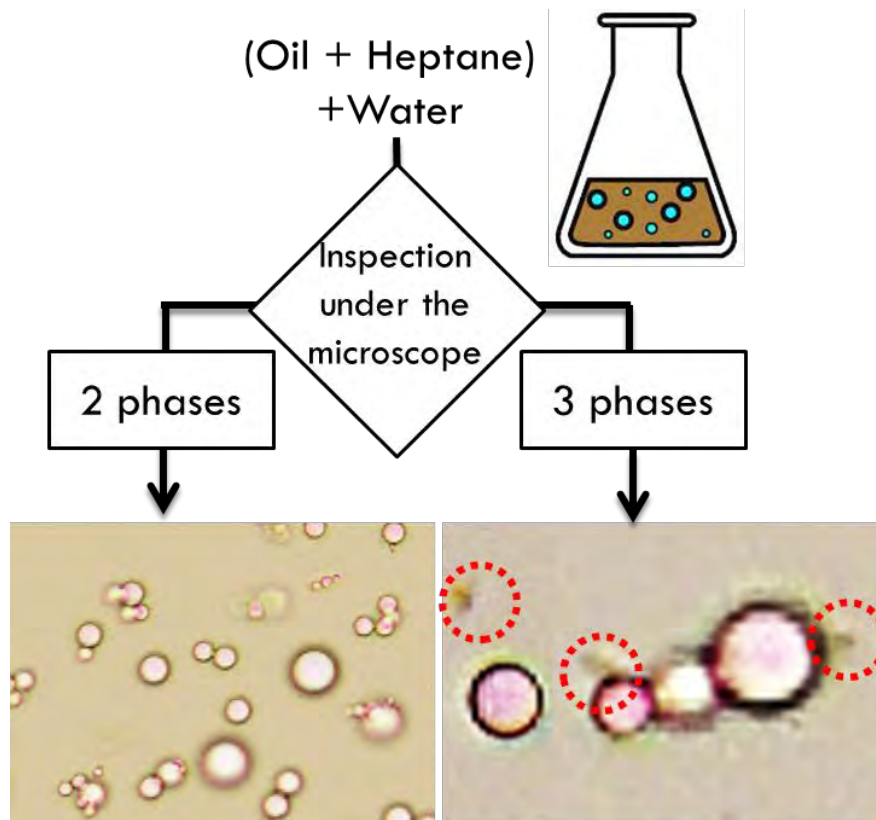


Figure 4.5 Uncertainty in detection time reading caused by three phases in one system.

4.2 Detection Time Experiment (Part II) – Centrifuged Oil + Water

The second part of the results will be proving that water does have effect on the rate of asphaltene aggregation by centrifuged the oil+10wt% water mixture and keep the supernatant for performing experiments. The experiment scheme is showed in Figure 4.6. The study is investigated further by performing higher number of centrifugation cycle (2nd, 3rd, and 4th round). IAA is expected to be removed after centrifugation and more when processes to each round of centrifugation.

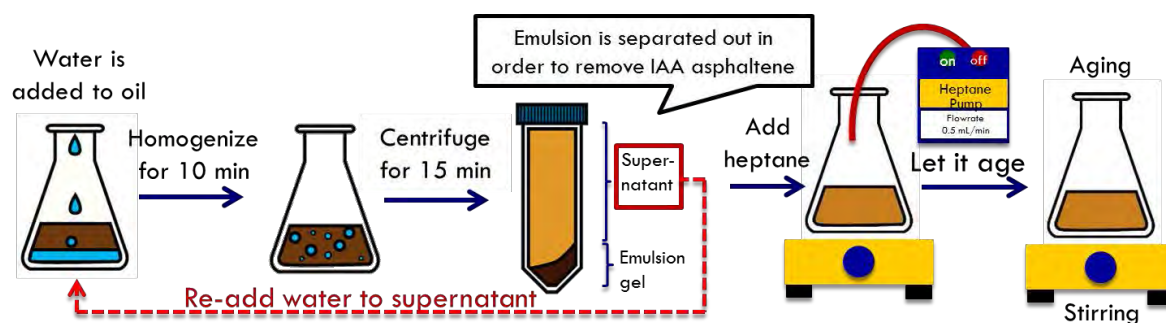


Figure 4.6 Experimental scheme part II.

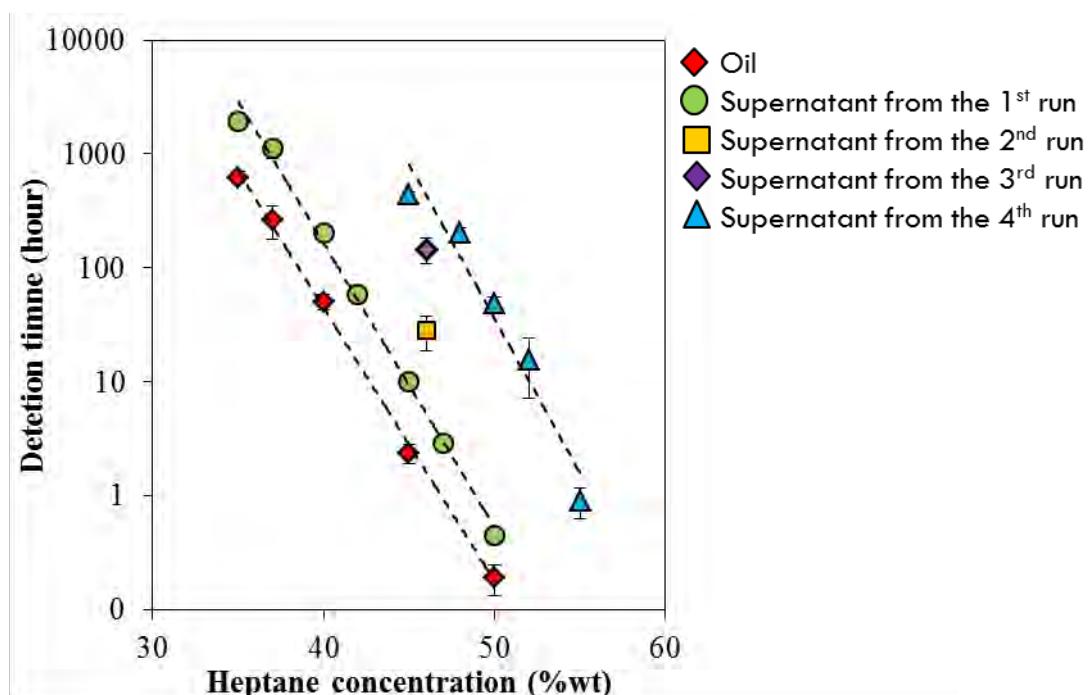


Figure 4.7 Rate of asphaltene aggregation compared between pure oil and supernatant obtained from each round of centrifugation.

From Figure 4.7, the rate of asphaltene of centrifuged oil+water becomes slower compared to the pure crude oil. As the heptane concentration decreases, it takes longer time for asphaltene to aggregate. When the oil-water mixture is centrifuged, some particles of interfacially active asphaltene might be drawn out as well as water molecules due to the fact that IAA is irreversibly attached to the water

interface. However, the hypothesis is not tested yet, until there is a clear evidence in the next part of the experiment.

The chemical properties of supernatant obtained from each round of centrifugation are tested and summarized in the Table 4.2. From the table, it could be summarized that the chemical properties do not seem to change with the presence of water.

Table 4.2 Chemical properties of the supernatant obtained from centrifugation

Properties	Unit	Pure oil	Supernatant			
			1 st	2 nd	3 rd	4 th
Density	g/cm ³	0.8634 ± 2.0E-04	0.8654 ± 2.0E-04	0.8687 ± 1.0E-04	0.8689 ± 1.0E-04	0.8679 ± 1.0E-04
Viscosity	Pa.s	0.015 ± 4.1E-03	0.015 ± 1.5E-02	0.015 ± 6.1E-03	0.016 ± 1.3E-02	0.016 ± 2.7E-03
Absorbance	AU	0.025 ± 1.0E-03	0.025 ± 1.0E-03	0.024 ± 1.0E-03	0.027 ± 2.0E-03	0.025 ± 1.0E-03
Refractive index		1.487 ± 2.9E-05	1.488 ± 7.7E-05	1.489 ± 7.7E-05	1.489 ± 2.9E-05	1.490 ± 1.5E-04
Solubility Parameter	MPa ^{1/2}	17.89 ± 1.5E-03	17.90 ± 4.0E-03	17.92 ± 4.0E-03	17.94 ± 1.5E-03	17.96 ± 8.0E-03

The only parameter that changed probably is the asphaltene content, shown in Figure 4.8. The results of the study show that the amount of asphaltene reduce in every centrifugation round which corresponds to the results from the detection time experiment. Nevertheless, the result is expected due to the fact that the IAA is irreversibly absorbed on the water interface and, as a result of centrifugation, IAA was drawn along with the water molecule. This could be the main cause of the shift in the detection time. With lower amount of asphaltene, the detection time shifts to the right, in other words, it takes longer time to be able to detect the appearance of asphaltene aggregation under microscope. From this conclusion, it confirms that water plays essential role in the rate of asphaltene aggregation, especially the IAA.

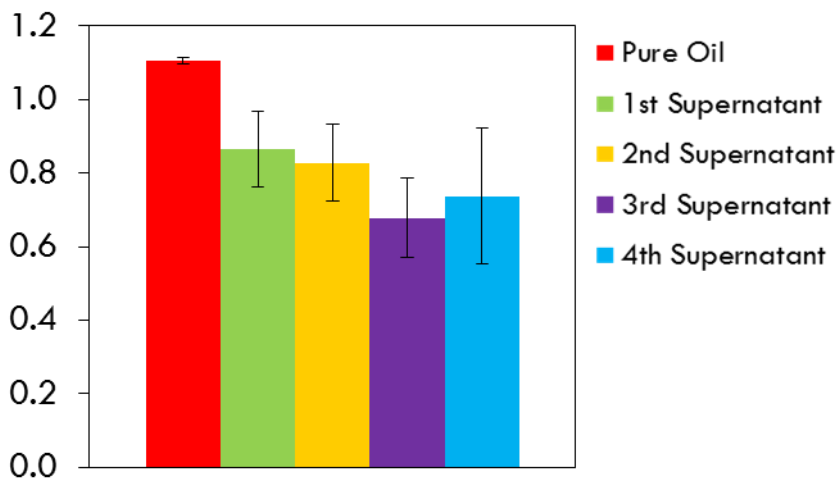


Figure 4.8 The asphaltene content of different centrifugation.

Not only the supernatant, but also the emulsion gel (centrifuged cake) is characterized. The amount of IAA is investigated in order to calculate surface density of asphaltene per gram of surface area. To do so, asphaltene (IAA) must be extracted from the emulsion gel; the gel is diluted with toluene in the fraction of 5 g of emulsion gel per 40 mL of toluene. Fundamentally, the toluene needed for dilution must be sufficient to extract all the NIAA asphaltene and the oil trapped in between water molecules and IAA; therefore, with 5 g in 40 mL of toluene should be able to dissolve all NIAA asphaltene from the emulsion gel. The solution (toluene + emulsion gel) is then kept shaking for approximately 10 minutes and then centrifuged afterwards for 15 minutes at 25 degree Celsius. The supernatant and the cake obtained from the centrifugation are separated from each other. The surface density of asphaltene on the interfacial area is calculated from the dried cake after 3 days of drying which equals to 0.018 gram per m^2 of interfacial area. Therefore, the amount of IAA removed from the total asphaltene is approximately 5.3%. The entire procedure of IAA extraction is shown in Figure 4.9.

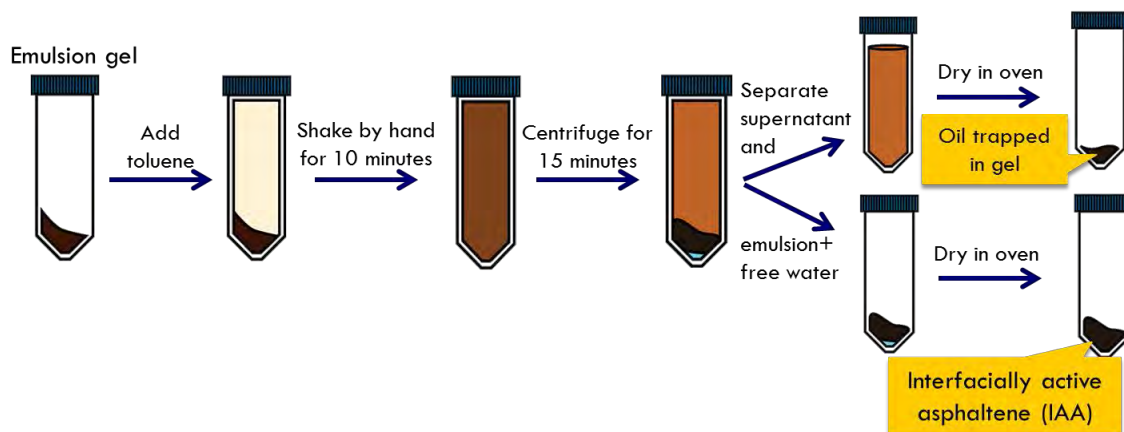


Figure 4.9 IAA extraction through toluene-washing process.

4.3 Detection Time Experiment (Part III) – Quantifying the Amount of Precipitated Asphaltenes

In this part, to be able to determine whether the water probably pull off some asphaltene aggregates, performing centrifugation and measure the amount of asphaltene precipitated is one method. The asphaltene that undergoes flocculation and can be separated out of the solution by centrifugation are known as unstable asphaltenes. The unstable asphaltene is most likely the problematic asphaltene that causes many petroleum facilities go under maintenance. The procedure starts from the preparing the mixture of oil and heptane (heptane is asphaltene induced chemicals) in a large quantity and then leave on the stir plate for a certain period of time (aging). While the oil and heptane mixture is aging, part of the solution is collected and then centrifuged for 10 minutes at 14,000 rpm in order to obtain the unstable asphaltene. The procedure is shown in Figure 4.10. The results of the experiments is shown in Figure 4.11 which composes of 3 experiments: oil, 1st supernatant and 2nd supernatant.

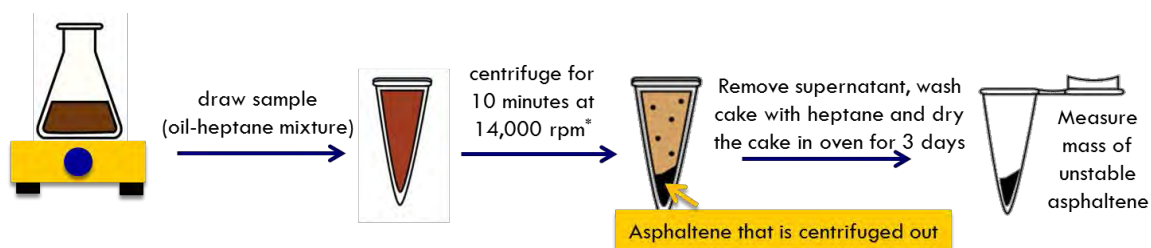


Figure 4.10 Quantifying the amount of unstable asphaltene via centrifugation.

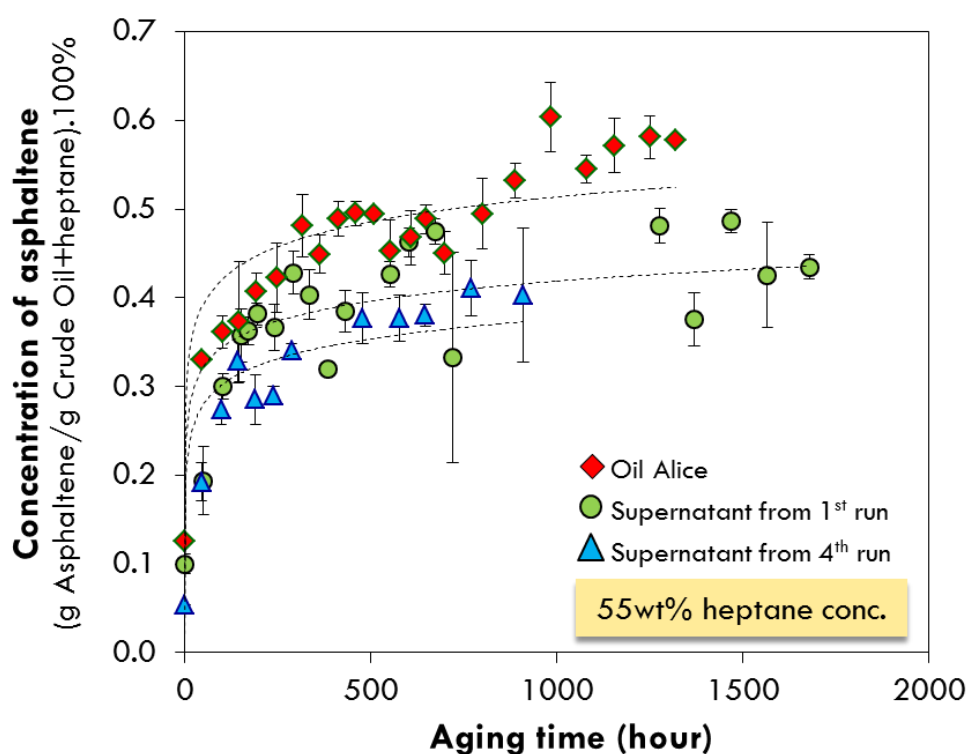


Figure 4.11 Concentration of asphaltene is plotted against the aging time at 55wt% heptane concentration.

The curves shown in Figure 4.11 is a strong evidence that shows that there is some asphaltene removed with water after centrifugation. The plateau values represent the amount of unstable asphaltene at a given heptane concentration (55wt%) which equals to 0.54%, 0.45% and 0.35% for pure oil, 1st supernatant and 4th supernatant respectively. It could be interpreted that as the oil contains water, the IAA irreversibly absorbs on the water-oil interface and, as more water is added to oil,

more IAA absorbed more on the interface. Therefore, the amount of unstable asphaltene is a strong experimental result used for support the statement that says asphaltene is a natural emulsifier and could form stable emulsions with water, and consequently of having water present in the oil, there is no asphaltene deposit on the metal surface of the pipeline.

4.4 Asphaltene Aggregation Model

Not only the fact that asphaltene (IAA) is removed when water is present, solubility of asphaltene is also another parameter that could not be taken for granted. According to asphaltene aggregation model proposed by Haji-Akbari et al (2013), A Unified Model for Aggregation of Asphaltenes, the rate of asphaltene aggregation is affected by the solubility parameter of asphaltene as well as the concentration of unstable asphaltene. The asphaltene aggregation model is written below as shown in equation 6.1. After obtaining detection time from different heptane concentration and other important parameters such as viscosity and solubility parameter of solution (oil-heptane solution), all the parameters are applied to the model in order to calculate the values of asphaltene solubility parameters by using the fitting-curve method. The result of fitting the model curve with experimental data is shown in Figure 4.12.

$$\ln\left(\frac{t_{\text{detection}}\sqrt{C_1(0)}}{\mu}\right) \propto \frac{1}{(\delta_{\text{asph}} - \delta_{\text{solution}})^2} \quad \text{Eq 6.1}$$

Where $t_{\text{detection}}$ - detection time (hour)

$C_1(0)$ - The concentration of asphaltene at a given heptane concentration

μ - viscosity of the solution (Pa.S)

δ_{asph} - solubility of asphaltene (MPa^{0.5})

δ_{solution} - solubility of solution (MPa^{0.5})

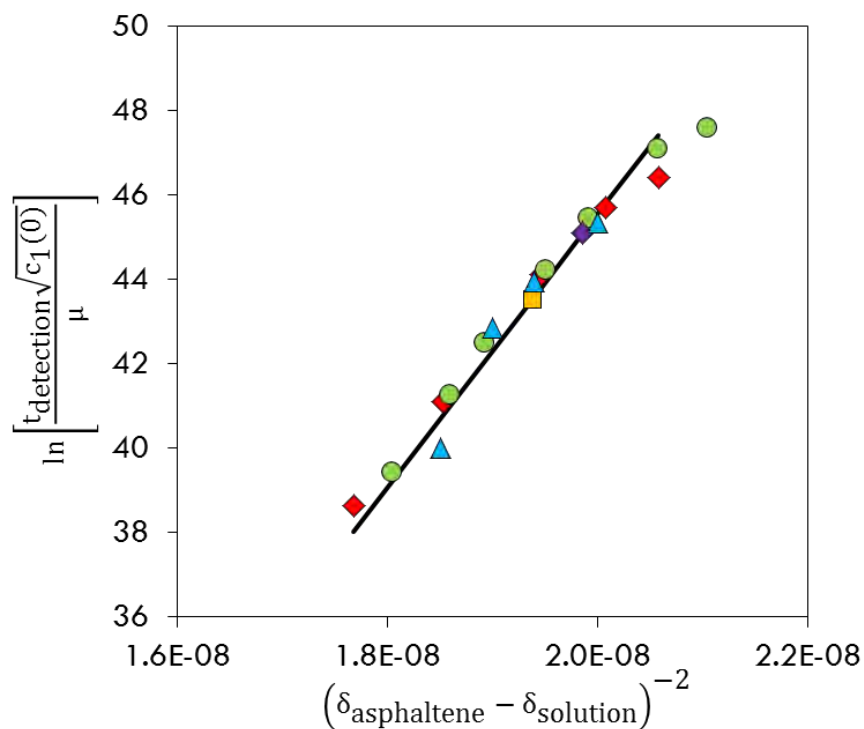


Figure 4.12 The fitting curve method of finding the solubility of asphaltene.

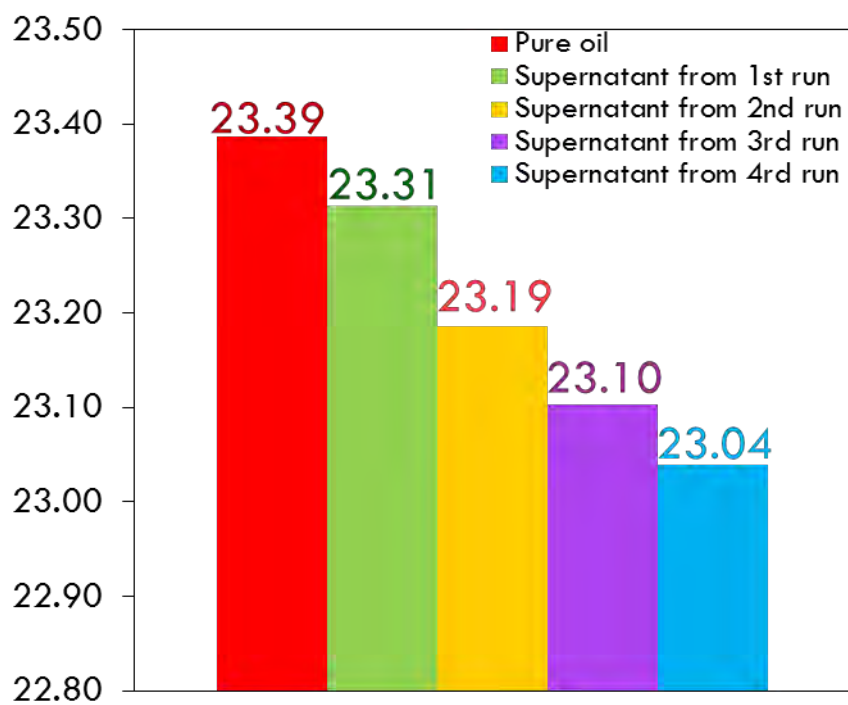


Figure 4.13 The solubility of asphaltene as a result from fitting curve method.

As it can be seen from Figure 4.13, the solubility of asphaltene decreases as the number of centrifugation increases which mean that when IAA is absorbed on the oil-water interface, the overall solubility of asphaltene is reduced. The result also suggests that IAA is on the high end of solubility parameter distribution of the studied oil. Therefore, another parameter that is affected with the water emulsion is solubility parameter of asphaltene.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The primary goal of this project is to investigate the effect of water emulsion on the rate of asphaltene aggregation. The experiment divided into 3 parts: 1) detection time on oil and oil+water, 2) detection time on supernatant obtained from centrifuged oil+10wt% water mixture, 3) asphaltene concentration quantification using centrifugation technique and 4.) asphaltene aggregation model. The first part is to study the rate of asphaltene aggregation by detecting the time asphaltene starts to aggregate and plotted against heptane concentration. The results from the first part of the experiment prove that water emulsion in oil does affect the asphaltene aggregation, both increasing and decreasing rate of asphaltene aggregation depending on water content. However, one question is raised due to the fact that there is an uncertainty on the detecting asphaltene aggregation when 3rd phase (water) is present in the solution and cannot differentiate under microscope.

The second part of the experiment is implemented from the 1st part of the experiment by adding additional step to the previous experiment using centrifugation technique to remove water from the solution. As a consequence of performing detection time experiment on the supernatant obtained from oil+10wt%water centrifugation. It was found that water might remove some of the problematic asphaltene or known as IAA along with the precipitated phase from centrifugation of 15 minutes at 14,000 rpm. The detection time curve of the supernatant shifted from the pure oil as a result of the reducing amount of asphaltene in the solution. To reconfirm the result, the experiment of finding concentration of asphaltene is carried out and the result shows that the with water presence, there is lower unstable asphaltene. The hypothesis of how this happens is that IAA is categorized as unstable asphaltene because it is considered to be the asphaltene that causes asphaltene to aggregated and deposit on the surface of metal pipeline and when it is separated out along with water molecules using centrifugation technique, IAA is removed and that results in shifts in detection time curve.

To prove this hypothesis, to quantify the amount of unstable asphaltene is the next step which comes to the experiment part III. From the result of plotting the graph

between asphaltene concentration and aging time, the amount of asphaltene from the case of centrifuged oil+10wt%water is almost twice as low as asphaltene obtained from pure oil. This leads to the conclusion that IAA is a part of unstable asphaltene and there is a delay in asphaltene deposition when those interfacially active asphaltene particles are centrifuged out from the whole asphaltene.

The experimental part IV used asphaltene aggregation model to explain the shift in the detection time experiment. The experimental data fits the master curve perfectly which means that Nasim's model can be used to explain the phenomena and, as a result, solubility parameter of asphaltene is calculated using the relationship from the model. The result shows that increase in the number of centrifugation will decrease the solubility parameter of asphaltene in the solution. This means that when IAA is removed, the solubility parameter of asphaltene becomes lower and can result in less asphaltene precipitation.

However, this study can be improved if there is a way to observe the asphaltene on the interface between water and oil phase. To be able to study the interface would provide more information to support the hypothesis and also uncover the truth about the asphaltene behavior on the interface. In addition, besides water, there are other factors related to asphaltene aggregation such as brine and wax which are also part of the reservoir. These parameters are poorly investigated and there are still some mysterious issues needed to be unlocked as well.

REFERENCES

- Al-Wahaibi, T., Al-Wahaibi, Y., Al-Hashmi, A.-A.R., Mjalli, F.S. and Al-Hatmi, S. (2015) Experimental investigation of the effects of various parameters on viscosity reduction of heavy crude by oil–water emulsion. Petroleum Science, 12(1), 170-176.
- Andersen, S.I., del Rio, J.M., Khvostitchenko, D., Shakir, S. and Lira-Galeana, C. (2001) Interaction and solubilization of water by petroleum asphaltenes in organic solution. Langmuir, 17(2), 307-313.
- Aslan, S. and Firoozabadi, A. (2014) Effect of water on deposition, aggregate size, and viscosity of asphaltenes. Langmuir, 30(13), 3658-3664.
- Bi, J., Yang, F., Harbottle, D., Pensini, E., Tchoukov, P., Simon, S., Sjoblom, J., Dabros, T., Czarnecki, J., Liu, Q. and Xu, Z. (2015) Interfacial layer properties of a polyaromatic compound and its role in stabilizing water-in-oil emulsions. Langmuir, 31(38), 10382-10391.
- Buckley, J.S. and Wang, J. (2002) Crude oil and asphaltene characterization for prediction of wetting alteration. Journal of Petroleum Science and Engineering, 33(1–3), 195-202.
- Carauta, A.N.M., Seidl, P.R., Chrisman, E.C.A.N., Correia, J.C.G., Menechini, P.d.O., Silva, D.M., Leal, K.Z., de Menezes, S.M.C., de Souza, W.F. and Teixeira, M.A.G. (2005) Modeling solvent effects on asphaltene dimers. Energy & Fuels, 19(4), 1245-1251.
- Chang, C.L. and Fogler, H.S. (1994) Stabilization of asphaltenes in aliphatic solvents using alkylbenzene-derived amphiphiles. 1. effect of the chemical structure of amphiphiles on asphaltene stabilization. Langmuir, 10(6), 1749-1757.
- Chang, C.L. and Fogler, H.S. (1994) Stabilization of asphaltenes in aliphatic solvents using alkylbenzene-derived amphiphiles. 2. study of the asphaltene-amphiphile interactions and structures using fourier transform infrared spectroscopy and small-angle x-ray scattering techniques. Langmuir, 10(6), 1758-1766.

- Enweremadu, C.C., Rutto, H.L. and Oladeji, J.T. (2011) Investigation of the relationship between some basic flow properties of shea butter biodiesel and their blends with diesel fuel. International Journal of the Physical Sciences, 6(4), 758-767.
- Fahim, M.A., Alsahhaf, T.A. and Elkilani, A. (2010) Fundamentals of petroleum refining, Amsterdam: Elsevier.
- French, D.J., Taylor, P., Fowler, J. and Clegg, P.S. (2015) Making and breaking bridges in a pickering emulsion. Journal of Colloid and Interface Science, 441(1), 30-38.
- Haji-Akbari, N., Masirisuk, P., Hoepfner, M.P. and Fogler, H.S. (2013) A unified model for aggregation of asphaltenes. Energy & Fuels, 27(5), 2497-2505.
- Haji-Akbari, N., Teeraphakul, P. and Fogler, H.S. (2014) Effect of asphaltene concentration on the aggregation and precipitation tendency of asphaltenes. Energy & Fuels, 28(2), 909-919.
- Hansen, C.M. (2007) Hansen solubility parameters: a user's handbook, Florida: CRC Press.
- Harbottle, D., Chen, Q., Moorthy, K., Wang, L., Xu, S., Liu, Q., Sjoblom, J. and Xu, Z. (2014) Problematic stabilizing films in petroleum emulsions: shear rheological response of viscoelastic asphaltene films and the effect on drop coalescence. Langmuir, 30(23), 6730-6738.
- Hoepfner, M.P., Favero, C.V., Haji-Akbari, N. and Fogler, H.S. (2013) The fractal aggregation of asphaltenes. Langmuir, 29(28), 8799-8808.
- Hu, C., Sabio, J.C., Yen, A., Joshi, N. and Hartman, R.L. (2015) Role of water on the precipitation and deposition of asphaltenes in packed-bed microreactors. Industrial & Engineering Chemistry Research, 54(16), 4103-4112.
- Kaminski, T.J., Fogler, H.S., Wolf, N., Wattana, P. and Mairal, A. (2000) Classification of asphaltenes via fractionation and the effect of heteroatom content on dissolution kinetics. Energy & Fuels, 14(1), 25-30.
- Khvostichenko, D.S. and Andersen, S.I. (2008) Interactions between asphaltenes and water in solutions in toluene. Energy & Fuels, 22(5), 3096-3103.

- Kilpatrick, P.K. (2012) Water-in-crude oil emulsion stabilization: review and unanswered questions. Energy & Fuels, 26(7), 4017-4026.
- Langevin, D., Poteau, S., Hénaut, I. and Argillier, J.F. (2004) Crude oil emulsion properties and their application to heavy oil transportation. Oil & Gas Science and Technology - Revue de l'IFP, 59(5), 511-521.
- Li, Z., Harbottle, D., Pensini, E., Ngai, T., Richtering, W. and Xu, Z. (2015) Fundamental study of emulsions stabilized by soft and rigid particles. Langmuir, 31(23), 6282-6288.
- Lian, H., Lin, J.R. and Yen, T.F. (1994) Peptization studies of asphaltene and solubility parameter spectra. Fuel, 73(3), 423-428.
- Maqbool, T., Raha, S., Hoepfner, M.P. and Fogler, H.S. (2011) Modeling the aggregation of asphaltene nanoaggregates in crude oil-precipitant systems. Energy & Fuels, 25(4), 1585-1596.
- Merdrignac, I. and Espinat, D. (2007) Physicochemical characterization of petroleum fractions: the state of the art. Oil & Gas Science and Technology - Revue de l'IFP, 62(1), 7-32.
- Mitchell, D.L. and Speight, J.G. (1973) The solubility of asphaltenes in hydrocarbon solvents. Fuel, 52(2), 149-152.
- Moeini, F., Hemmati-Sarapardeh, A., Ghazanfari, M.-H., Masihi, M. and Ayatollahi, S. (2014) Toward mechanistic understanding of heavy crude oil/brine interfacial tension: The roles of salinity, temperature and pressure. Fluid Phase Equilibria, 37(5), 191-200.
- Moradi, M., Alvarado, V. and Huzurbazar, S. (2011) Effect of salinity on water-in-crude oil emulsion: evaluation through drop-size distribution proxy. Energy & Fuels, 25(1), 260-268.
- Mullins, O.C. and Sheu, E.Y. (1999) Structures and dynamics of asphaltenes, New York: Plenum Press.
- Murgich, J. (2002) Intermolecular forces in aggregates of asphaltenes and resins. Petroleum Science and Technology, 20(9-10), 983-997.
- Murgich, J., Merino-Garcia, D., Andersen, S.I., Del Río, J.M. and Galeana, C.L. (2002) Molecular mechanics and microcalorimetric investigations of the

- effects of molecular water on the aggregation of asphaltenes in solutions. Langmuir, 18(23), 9080-9086.
- Murgich, J., Rodríguez, J.M. and Aray, Y. (1996) Articles molecular recognition and molecular mechanics of micelles of some model asphaltenes and resin. Energy & Fuels, 10(1), 68-76.
- Nalwaya, V., Tantayakom, V., Piumsomboon, P. and Fogler, S. (1999) Studies on asphaltenes through analysis of polar fractions. Industrial & Engineering Chemistry Research, 38(3), 964-972.
- Nour, A.H. and Yunus, R.M. (2006) Stability investigation of water-in-crude oil emulsion. Journal of Applied Sciences, 6(14), 2895-2900.
- Porte, G., Zhou, H. and Lazzeri, V. (2003) Reversible description of asphaltene colloidal association and precipitation. Langmuir, 19(1), 40-47.
- Poteau, S., Argillier, J.F., Langevin, D., Pincet, F. and Perez, E. (2005) Influence of pH on stability and dynamic properties of asphaltenes and other amphiphilic molecules at the oil-water interface. Energy & Fuels, 19(4), 1337-1341.
- Qiao, P., Harbottle, D., Tchoukov, P., Masliyah, J., Sjöblom, J., Liu, Q. and Xu, Z. (2017) Fractionation of asphaltenes in understanding their role in petroleum emulsion stability and fouling. Energy & Fuels, 31(4), 3330-3337.
- Rane, J.P., Harbottle, D., Pauchard, V., Couzis, A. and Banerjee, S. (2012) Adsorption kinetics of asphaltenes at the oil-water interface and nanoaggregation in the bulk. Langmuir, 28(26), 9986-9995.
- Rane, J.P., Pauchard, V., Couzis, A. and Banerjee, S. (2013) Interfacial rheology of asphaltenes at oil-water interfaces and interpretation of the equation of state. Langmuir, 29(15), 4750-4759.
- Sheu, E.Y. and Mullins, O.C. (1995) Asphaltenes: fundamentals and applications, New York: Plenum Press.
- Sjöblom, J., Aske, N., Harald Auflem, I., Brandal, Ø., Erik Havre, T., Sæther, Ø., Westvik, A., Eng Johnsen, E. and Kallevik, H. (2003) Our current understanding of water-in-crude oil emulsions. Advances in Colloid and Interface Science, 100-102, 399-473.

- Speight, J. (1982) The chemistry and technology of petroleum, New York: Marcel Dekker.
- Spiecker, P.M., Gawrys, K.L. and Kilpatrick, P.K. (2003) Aggregation and solubility behavior of asphaltenes and their subfractions. Journal of Colloid Interface Science, 267(1), 178-193.
- Spiecker, P.M., Gawrys, K.L., Trail, C.B. and Kilpatrick, P.K. (2003) Effects of petroleum resins on asphaltene aggregation and water-in-oil emulsion formation. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 220(1-3), 9-27.
- Spiecker, P.M. and Kilpatrick, P.K. (2004) Interfacial rheology of petroleum asphaltenes at the oil-water interface. Langmuir, 20(10), 4022-4032.
- Strausz, O.P., Torres, M., Lown, E.M., Safarik, I. and Murgich, J. (2006) Equipartitioning of precipitant solubles between the solution phase and precipitated asphaltene in the precipitation of asphaltene. Energy & Fuels, 20(5), 2013-2021.
- Tan, X., Fenniri, H. and Gray, M.R. (2009) Water enhances the aggregation of model asphaltenes in solution via hydrogen bonding. Energy & Fuels, 23(7), 3687-3693.
- Tavakkoli, M., Chen, A., Sung, C.-A., Kidder, K.M., Lee, J.J., Alhassan, S.M. and Vargas, F.M. (2016) Effect of emulsified water on asphaltene instability in crude oils. Energy & Fuels, 30(5), 3676-3686.
- Tharanivasan, A.K. (2012) Asphaltene precipitation from crude oil blends, conventional oils, and oils with emulsified water. Ph.D. Thesis, Department of chemical and petroleum engineering, University of Calgary, Calgary, Canada.
- Tharanivasan, A.K., Yarranton, H.W. and Taylor, S.D. (2012) Asphaltene Precipitation from Crude Oils in the Presence of Emulsified Water. Energy & Fuels, 26(11), 6869-6875.
- Vananton, H.W. (1997) Asphaltene Solubility and Asphaltene Stabilized Water-in-Oil Emulsions. Ph.D. Thesis, Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Canada.

- Verruto, V.J. and Kilpatrick, P.K. (2008) Water-in-model oil emulsions studied by small-angle neutron scattering: Interfacial film thickness and composition. Langmuir, 24(22), 12807-12822.
- Yang, F., Tchoukov, P., Dettman, H., Teklebrhan, R.B., Liu, L., Dabros, T., Czarnecki, J., Masliyah, J. and Xu, Z. (2015) Asphaltene subfractions responsible for stabilizing water-in-crude oil emulsions. part 2: molecular representations and molecular dynamics simulations. Energy & Fuels, 29(8), 4783-4794.
- Yang, F., Tchoukov, P., Pensini, E., Dabros, T., Czarnecki, J., Masliyah, J. and Xu, Z. (2014) Asphaltene subfractions responsible for stabilizing water-in-crude oil emulsions. part 1: interfacial behaviors. Energy & Fuels, 28(11), 6897-6904.
- Yen, T.F. and Chilingarian, G.V. (1994) Asphaltenes and asphalts, Amsterdam: Elsevier Science.

APPENDIX

Solubility Parameter of Asphaltene Calculation

According to Nasim's asphaltene aggregation model, there are four parameters needed to know in order to solve for solubility parameter of asphaltene which are 1) detection time (time of first asphaltene appearance in hour), 2) concentration of unstable asphaltene calculated in term of mole of asphaltene per m³ solution, 3) viscosity of solution (Pa.s) and 4) solubility parameter of asphaltene.

$$\ln \left(\frac{t_{detection} \sqrt{C_1(0)}}{\mu} \right) = \frac{3.2453 \times 10^9}{(\delta_{asph} - \delta_{solution})^2} - 19.3564 \quad \text{Eq.1}$$

The detection time can be found from experiments which are described in the experimental procedure sections. For the concentration of unstable asphaltene, it is calculated using the plateau value obtained from a function between grams of asphaltene per 100 g of solution and time dependence. Viscosity of solution can be measured using different techniques but, for this study, rheometer was used.

However, $C_1(0)$ can be obtained if plateau values of at least 2 heptane concentrations are known but if only one heptane concentration is known, starting from 0 would be the closet estimation (figure 1).

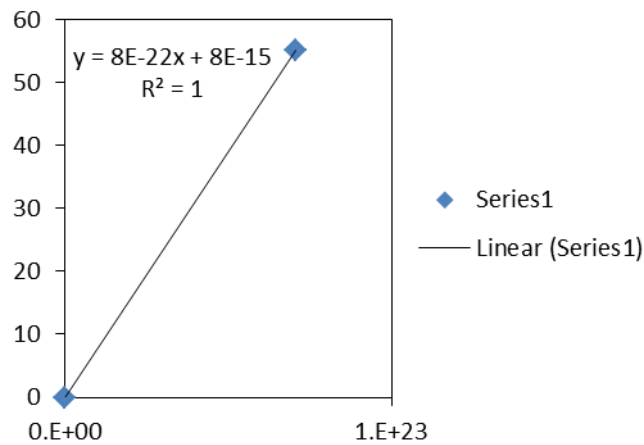


Figure 1 Calculating $C_1(0)$ as a function of heptane concentration.

After obtaining $C_1(0)$ as a function of heptane concentration and detection time from experiments, another important parameter needed to know is solubility of solution. It is calculated using summation of parameter solubility of each component times with its volume as it is written below.

$$\delta_{\text{solution}} = \delta_1 V_1 + \delta_2 V_2 \quad \text{Eq.2}$$

Where number represents each component in mixture

“1” represents one component which in this case is oil

“2” represents another component which in this case is heptane

Now, only one parameter is unknown left in the Nasim's equation which is solubility parameter of asphaltene. The method of finding solubility parameter is to use a technique called square error using Nasim's equation as a master curve and then try to fit the experimental data with her equation. In this thesis, the technique is illustrated in steps as following.

1. List all the experimental data needed in the equation which composed of detection time, $C_1(0)$ as a function of heptane concentration, viscosity and solubility parameter of solutions

$$\ln \left(\frac{t_{\text{detection}} \sqrt{C_1(0)}}{\mu} \right) = \frac{3.2453 \times 10^9}{(\delta_{\text{asph}} - \delta_{\text{solution}})^2} - 19.3564$$

Heptane concentration (wt%)	Detection time (hr)	$C_1(0)$ based on heptane concentration (mole of asp/m ³ of solution)	δ_{solution} (MPa) ^{1/2}	Experimental data (using left term of Nasim's equation)	$\delta_{\text{asphaltene}}$ (MPa) ^{1/2}	Nasim's Master curve (using right term of Nasim's equation)	square error (Exp-Master's curve) ²
1							
2							
3							
4							
5							

Figure 2 Calculation table example for finding δ_{asph} .

$$\ln \left(\frac{t_{\text{detection}} \sqrt{C_1(0)}}{\mu} \right) = \frac{3.2453 \times 10^9}{(\delta_{\text{asph}} - \delta_{\text{solution}})^2} - 19.3564$$

Heptane concentration (wt%)	Detection time (hr)	$C_1(0)$ based on heptane concentration (mole of asp/m ³ of solution)	δ_{solution} (MPa) ^{1/2}	Experimental data (using left term of Nasim's equation)	$\delta_{\text{asphaltene}}$ (MPa) ^{1/2}	Nasim's Master curve (using right term of Nasim's equation)	square error (Exp-Master's curve) ²
1	50	2	6.4262E+22	15.8648	38.6274	23.3864	0.3848
2	45	5	5.7836E+22	16.0385	41.0965	**Set random value at the beginning and using solve to find the value that makes the least square error	0.1190
3	40	30	5.1409E+22	16.2173	44.1028		0.1003
4	35	80	4.7554E+22	16.3283	45.7142		0.0056
5	30	200	4.4983E+22	16.4156	46.4226		1.0144
Summation						1.6241	

Figure 3 Calculation table example for finding δ_{asph} .

2. After filling all necessary data, the left term of Nasim's equation is used to calculate fitting curve (experimental curve) and the right term is for master's curve knowing that the parameter $\delta_{\text{asphaltene}}$ is randomly set at the beginning which will be left to be solved later after obtaining least square error

3. Calculate square error using experimental curve subtracts from master's curve and the square the product
4. Using function 'solve' in excel to find the least square error in order to find the real value of $\delta_{\text{asphaltene}}$
5. The graph between experimental data and master's curve against square error is used to see how closed those 2 values are as illustrated below (where the bold line represents the master's curve and the dots are for experimental data)

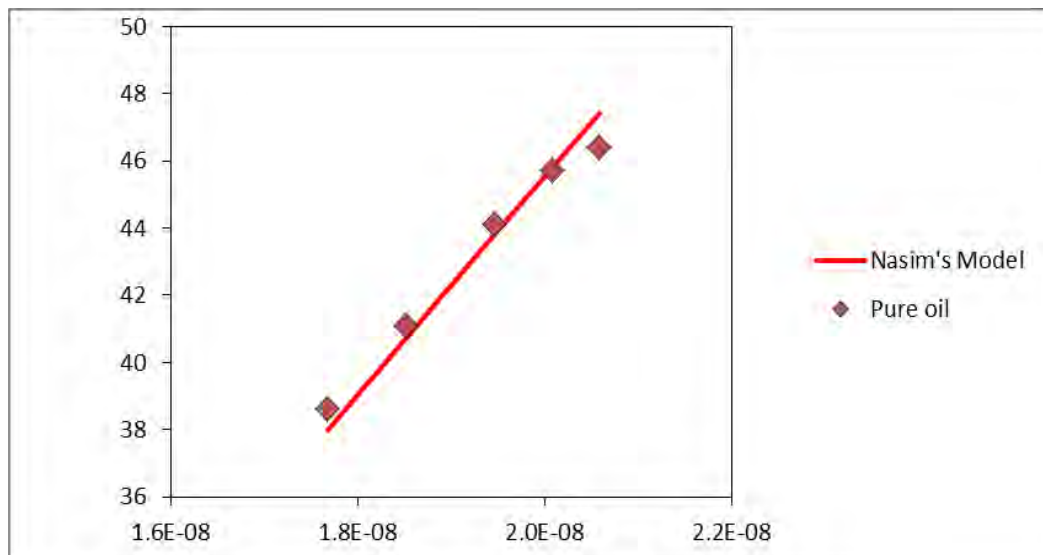


Figure 4 Calculating $C1(0)$ as a function of heptane concentration.

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1. Roengsamut P., Vilas Bôas Fávero C., Malakul P., and Fogler H. S. (2017, May 23rd) Investigation of asphaltene aggregation kinetics in the presence of water-in-oil emulsion. Proceedings of the 8th Research Symposium on Petrochemical and Material Technology and the 23rd PPC Symposium on Petroleum, Petrochemicals and Polymers, Bangkok, Thailand.