

**EFFECTS OF BEAD SIZE AND CONCENTRATION OF UNSTABLE  
ASPHALTENES OBTAINED FROM DIFFERENT CENTRIFUGATION  
TECHNIQUES ON ASPHALTENE DEPOSITION  
IN PACKED BED APPARATUS**

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**Thesis Title:** Effects of Bead Size and Concentration of Unstable Asphaltenes Obtained from Different Centrifugation Techniques on Asphaltene Deposition in Packed Bed Apparatus  
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**Program:** Petrochemical Technology  
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**ABSTRACT**

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Kimchhay Lao: Effects of Bead Size and Concentration of Unstable Asphaltenes Obtained from Different Centrifugation Techniques on Asphaltene Deposition in Packed Bed Apparatus.

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Asphaltenes are the heaviest and most polar fraction of petroleum crude oil. They are the collection of components that can be soluble in aromatics solvents such as benzene or toluene, but insoluble in normal alkanes, n-pentane, n-hexane, or n-heptane. Asphaltenes are a class of molecules consisted of grouped aromatic rings with alkane chains. Changing pressure, temperature, composition, and shear rate during transportation can cause precipitation and deposition, resulting in reduced reservoir productivity due to restricted flow lines, fouling and blockages in the pore spaces of the reservoir. The goal of this investigation is to assess validity of two aspects of the packed bed asphaltene deposition methodology and model. The first aspect is on the validity of diffusion coefficient used in the deposition model with respect to bead size in packed bed; the second aspect is on the relationship between the concentration of unstable asphaltenes, the method to measure this concentration, and the deposition rate. In the first part, it was observed that the deposition rate increases as the bead size decreases, as is predicted by the diffusion-limited deposition model used. In the second part, results indicate that concentration of unstable asphaltenes based on long time centrifugation of fresh oil-heptane mixture is the appropriate scaling for asphaltene deposition rate, instead of aged oil-heptane mixtures.

## บทคัดย่อ

กิมชาย เล่า : ผลกระทบของขนาดลูกทรงกลมเหล็ก และความเข้มข้นของแอสฟัลทีนที่ไม่เสถียรที่ได้จากวิธีการเหวี่ยงที่แตกต่างกันต่อการเกาะติดของแอสฟัลทีนในแพคเบด (Effects of Bead Size and Concentration of Unstable Asphaltenes Obtained from Different Centrifugation Techniques on Asphaltene Deposition in Packed Bed Apparatus) อ. ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร. ปมทอง มาลากุล ณ อยุธยา และศาสตราจารย์ เอช สกอตต์ ฟอกเลอร์ 78 หน้า

แอสฟัลทีนเป็นหนึ่งในองค์ประกอบที่หนักและมีขี้ที่สุดของน้ำมัน แอสฟัลทีนสามารถละลายได้ในสารจำพวกอะโรมาติกอย่างเช่น เบนซีน และโทลูอินแต่ไม่สามารถละลายได้ในสารจำพวกนอร์มอลแอลเคนเช่น นอร์มอลเพนเทน และ นอร์มอลเฮปเทน โครงสร้างของโมเลกุลแอสฟัลทีนประกอบด้วยกลุ่มอะโรมาติก และสายโซ่แอลเคน โดยกระบวนการเปลี่ยนแปลงความดัน อุณหภูมิ องค์ประกอบ และแรงเฉือนระหว่างทำการขนส่ง สามารถทำให้เกิดการตกตะกอน และการเกาะติดของแอสฟัลทีนได้ ส่งผลให้ผลผลิตลดลงเนื่องจากมีข้อจำกัดของการไหลของของเหลว และการอุดตันในรูของแหล่งเก็บสะสมน้ำมัน วัตถุประสงค์ของศึกษานี้คือการตรวจสอบผลกระทบสองรูปแบบของวิธีการและแบบจำลองของการเกาะติดของแอสฟัลทีน รูปแบบที่หนึ่งคือการตรวจสอบค่าสัมประสิทธิ์การแผ่ที่ใช้ในการทำแบบจำลองของกระบวนการการเกาะติดของแอสฟัลทีนที่สอดคล้องกับขนาดของทรงกลมเหล็กที่แตกต่างในแพคเบด รูปแบบที่สองการหาความสัมพันธ์ระหว่างความเข้มข้นของแอสฟัลทีนที่ไม่เสถียร วิธีการวัดความเข้มข้นนั้น และอัตราการเกาะติด ส่วนที่หนึ่งค้นพบได้ว่าอัตราการเกาะติดเพิ่มขึ้นเมื่อขนาดของทรงกลมเหล็กลดลงซึ่งเป็นไปตามการคาดเดาโดยแบบจำลองการจำกัดการแผ่การเกาะติดที่ใช้ ส่วนที่สองผลได้แสดงให้เห็นว่าความเข้มข้นของแอสฟัลทีนที่ไม่เสถียรได้จากการเหวี่ยงของส่วนผสมน้ำมันและเฮปเทนที่สวดที่เวลานานเหมาะสมสำหรับการกระบวนการการเกาะติดของแอสฟัลทีนมากกว่าความเข้มข้นของแอสฟัลทีนที่ไม่เสถียรได้จากการเหวี่ยงของส่วนผสมน้ำมันและเฮปเทนที่ปล่อยทิ้งไว้ตามเวลา

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## CHAPTER I

### INTRODUCTION

Asphaltenes are the heaviest and most polar fraction of petroleum crude oil. They are the collection of components that can be soluble in aromatics solvents such as benzene or toluene, but insoluble in normal alkanes, n-pentane, n-hexane, or n-heptane. Asphaltenes are a class of molecules consisted of grouped aromatic rings with alkane chains. Some rings may be nonaromatic. Many of rings are fused, sharing at least one side of the rings. Heteroatoms, such as N, S, and O possibly connected in the aromatic rings can give the molecule polarity. Some researchers view phase behavior of asphaltenes as a liquid-liquid concentration fluctuation, but some postulate asphaltenes as small solid nanosized colloidal particles (Simanzhenkov *et al.*, 2003; Maqbool *et al.*, 2009; Hoepfner *et al.*, 2013; Haji-Akbari *et al.*, 2013; Mullins *et al.*, 2012).

Changing pressure, temperature, composition, and shear rate can cause precipitation and deposition. The precipitated asphaltenes from any point of oil production of reservoir crude oils or transportation can clog pipelines and production facilities, reduce storage capacity, cause equipment fouling and catalyst deactivation (Haji-Akbari *et al.*, 2013; Zhang *et al.*, 2007).

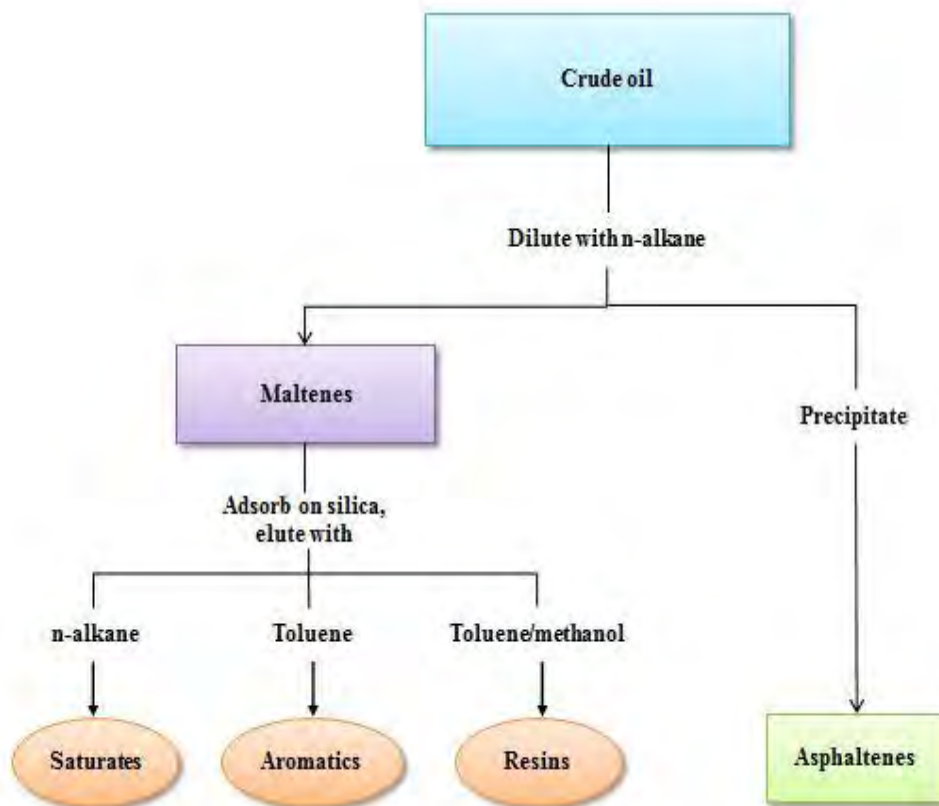
Many of research works have been focused on kinetics of asphaltenes precipitation and deposition mechanism. Precipitation can occur even though the concentration of heptane significantly below the instantaneous onset point, the concentration above which the precipitation kinetics are very fast. Below this concentration, the precipitation is very slow (Hoepfner *et al.*, 2013). Kinetics of asphaltenes can be further studied using centrifugation technique of precipitated asphaltenes in aged oil-heptane mixture (Maqbool *et al.*, 2009). Diffusion-limited deposition model has been used mostly on effect of flow rate to predict asphaltene deposition with heptane addition in packed bed apparatus. The relationship between specific deposition rate and concentration of unstable asphaltenes has been revealed that the rate is negative while the concentration is reaching zero (Vilas Bôas Fávero *et al.*, 2016).

The goal of this research will focus on investigating of effects of bead size and concentration of unstable asphaltenes obtained from different centrifugation techniques on asphaltene deposition in packed bed apparatus.

## CHAPTER II LITERATURE REVIEW

### 2.1 Crude Oil

Crude oil is a naturally occurring, unrefined petroleum product or complex mixture of hydrocarbons composing a variety of components with different physical and chemical properties. Often these components of the oil are divided into four major fractions: saturates aromatics, resins, and asphaltthenes (SARA). At the elemental level, it contains of elements such as carbon (84-87%) and hydrogen (12-14%) as well as oxygen, nitrogen and sulfur (1-2%) (Simanzhenkov *et al.*, 2003; Maqbool *et al.*, 2009). Separating crude oil into SARA by various methods is shown in Figure 2.1.



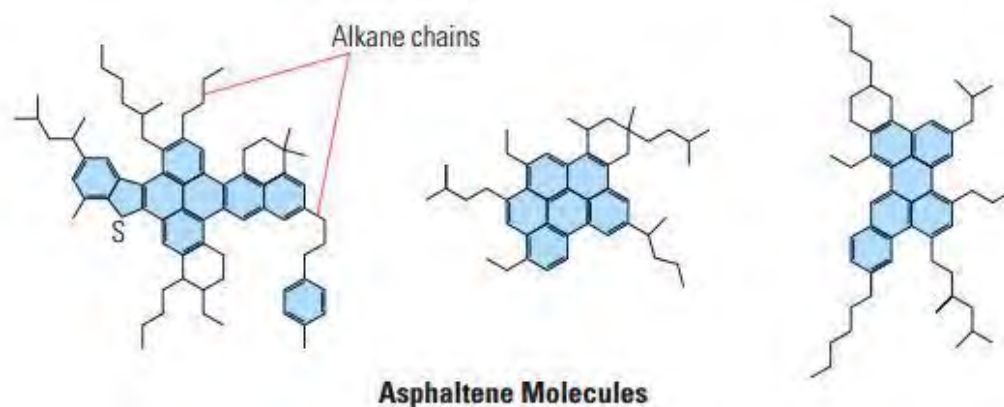
**Figure 2.1** Separating crude oil into SARA (Zhang *et al.*, 2007).



## 2.2 Asphaltenes

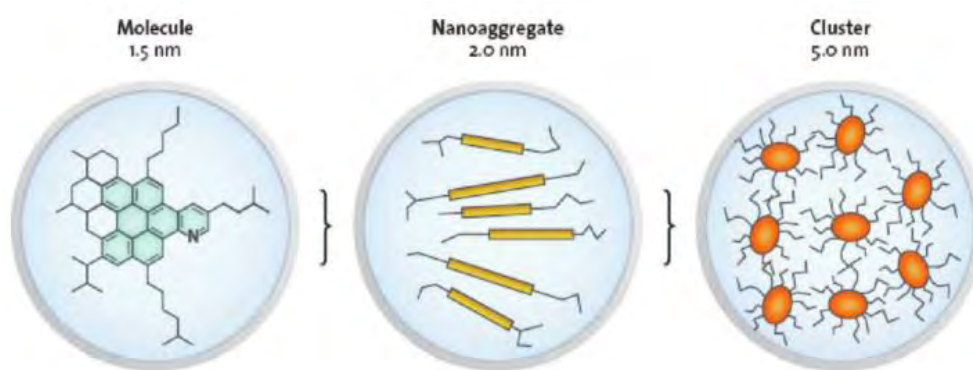
Asphaltenes are the heaviest and most polar fraction of petroleum crude oil. They are the collection of components that can be soluble in aromatics solvents such as benzene or toluene, but not insoluble in normal alkanes, n-pentane, n-hexane, or n-heptane. The most probable asphaltene molecular weight is  $\sim 750$ g/mol (Da). They comprise of polycyclic aromatic hydrocarbons with a random distribution of heteroatoms (e.g., N, S, O) and trace metals (e.g., V, Ni, Fe). Because there is the complexity of asphaltenes, their structure and natural state is still unclear. Some researcher view phase behavior of asphaltenes as a liquid-liquid concentration fluctuation, but some postulate asphaltenes as small solid nanosized colloidal particles (Maqbool *et al.*, 2009; Hoepfner *et al.*, 2013; Haji-Akbari *et al.*, 2013; Mullins *et al.*, 2012).

Asphaltenes are a class of molecules consisted of grouped aromatic rings with alkane chains. Some rings may be nonaromatic. Many of rings are fused, sharing at least one side of the rings. Heteroatoms possibly connected in the aromatic rings can give the molecule polarity. The polarizability of the fused aromatic-ring systems and the charge separation induced by heteroatoms cause the centers of neighboring asphaltene molecules to joint to each other, while the outer chains are repulsed by the chains of other molecules. Some asphaltenes consist of multiple groups of rings linked by alkane chains as shown in Figure 2.2.



**Figure 2.2** Three of many possible structures of asphaltenes (Zhang *et al.*, 2007).

In consistent with The “Yen-Mullins model”, proposing that the dominant molecular and colloidal structures of asphaltenes in laboratory solvents and crude oils are “island” molecular architecture, which polycyclic aromatic hydrocarbons (PAHs) are in the center as a core surrounded by alkyl groups. These molecules can form nanoaggregates with sufficient concentration, and can further form clusters with higher concentrations as shown in Figure 2.3.

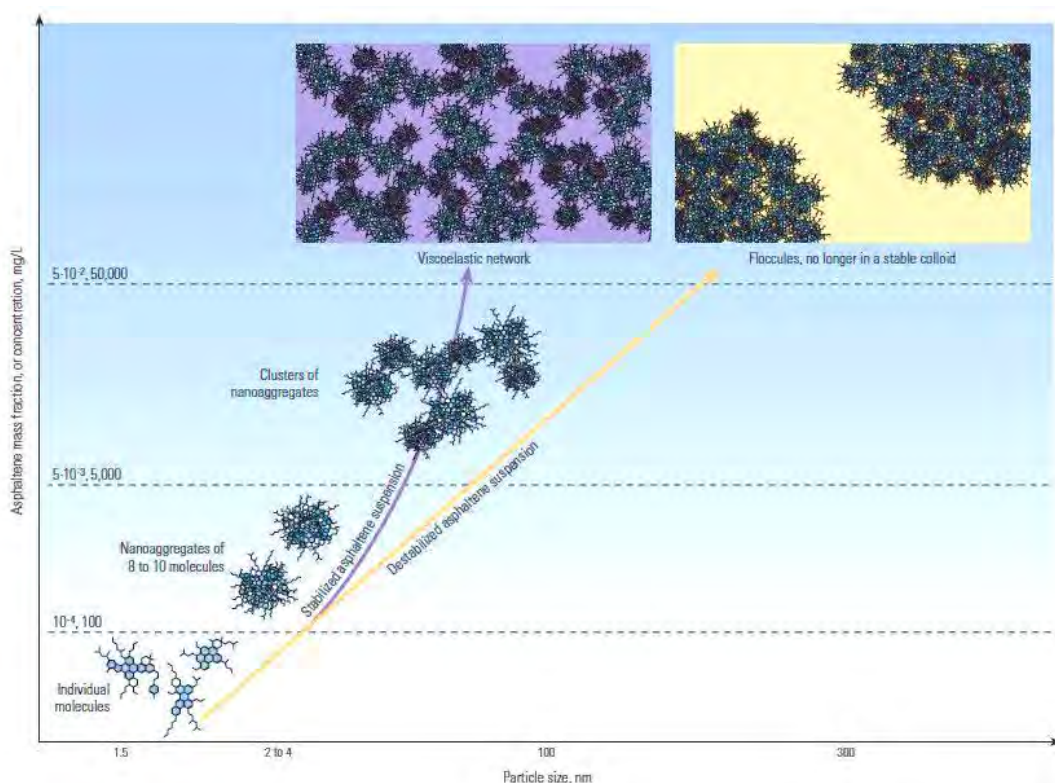


**Figure 2.3** Yen-Mullins model shows the structure for asphaltene molecules (Mullins *et al.*, 2012).

### 2.3 Asphaltene Aggregation and Precipitation

To be consistent and clear understanding, several terms of terminology are defined. “Destabilization” is refer to the development of an asphaltene in nanometer length scale from stable (not able to aggregate or grow in size) to unstable (able to aggregate or grow in size). In other words, destabilization is the phase separation or increase in aggregation tendency of nanoparticles and followed by collision and eventual aggregation of asphaltene nanoparticles into aggregates that can be detected under optical microscopy. “Aggregation” refers to the process of increasing the size of an asphaltene from nanometer to micrometer length scale. The whole process from stable asphaltene to micrometer –sized asphaltene aggregates or precipitates called “precipitation” (Hoepfner *et al.*, 2013; Haji-Akbari *et al.*, 2013).

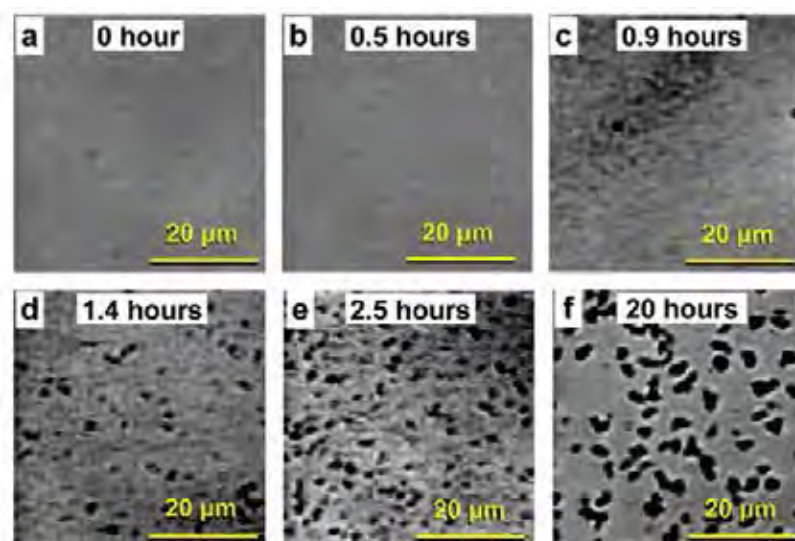
Aggregation behavior of asphaltenes depends on the concentration of asphaltenes. At low concentration, asphaltene molecules are seen to be individual molecules. As concentration increases, molecules stick together, initially in pairs, subsequently in larger number. Once concentration goes higher, the molecules form near-spherical nanoaggregates of eight to ten molecules stacked together and further form clusters, in which the bodies of the nanoaggregates do not overlap, but the alkane chains of neighboring clusters may interact. These clusters may remain in stable colloidal suspension until concentration reaches a mass fraction of  $5 \cdot 10^{-2}$ . Stability can continue to even higher concentration in crude oil, where clusters may form a viscoelastic network. In contrast, in toluene, high concentrations cause the asphaltene clusters to flocculate as shown in Figure 2.4.



**Figure 2.4** A transition of aggregation behavior of asphaltenes versus asphaltene concentration (Zhang *et al.*, 2007).

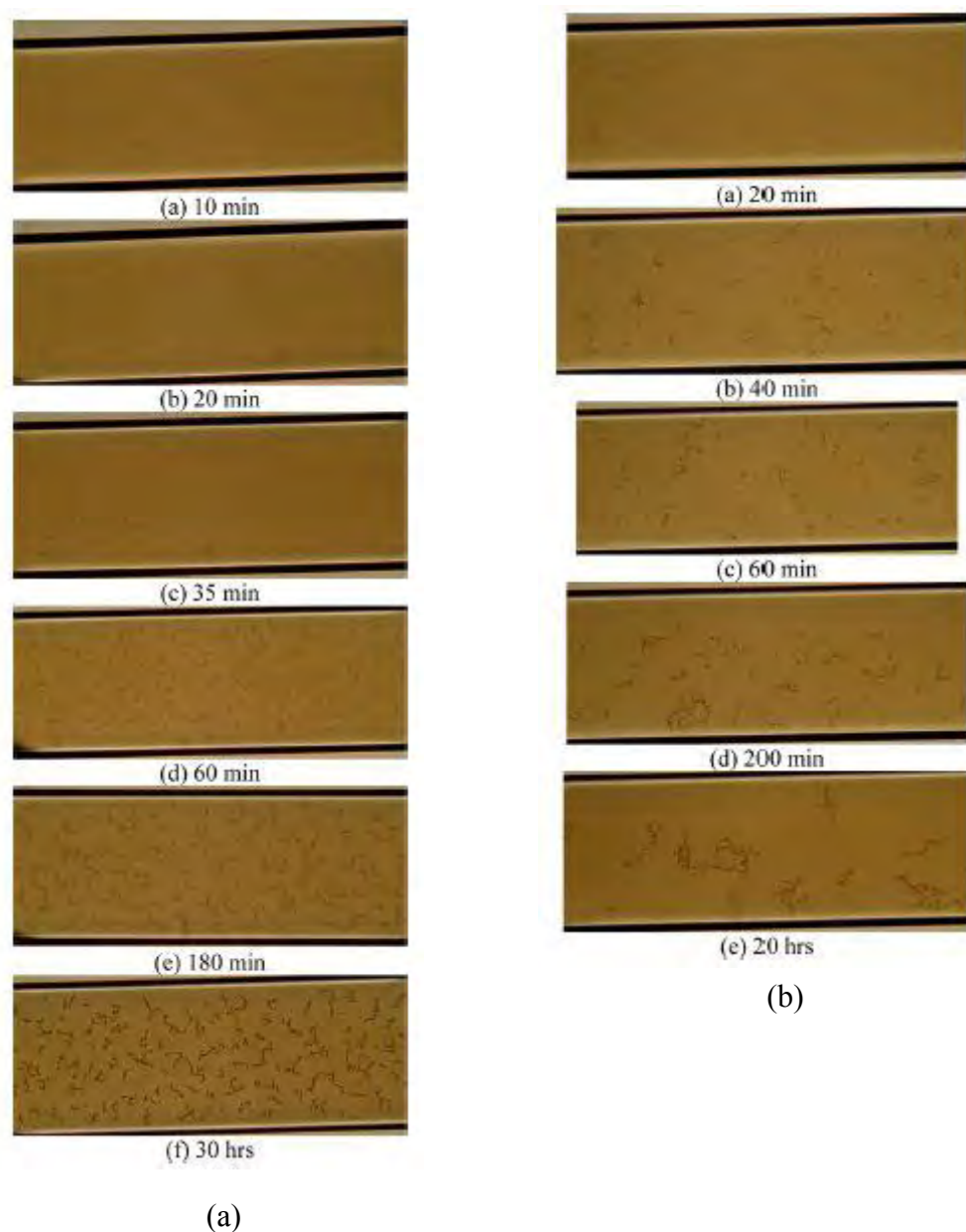
Typically, asphaltenes contain in crude oil as stable molecules. They can be destabilized to precipitate by changing pressure, temperature, composition, and shear rate. The precipitated asphaltenes from any point of oil production of reservoir crude oils or transportation can clog pipelines and production facilities, reduce storage capacity, and cause equipment fouling and catalyst deactivation (Haji-Akbari *et al.*, 2013; Zhang *et al.*, 2007). In experiment, researchers prefer to destabilize asphaltenes by adding n-alkane such as n-pentane and n-heptane directly to crude oil or mixture of asphaltenes and toluene called “model Oil” or “model fluid system” rather than others (Gon *et al.*, 2016; Boek *et al.*, 2008).

To study the destabilization of asphaltenes by adding different precipitants and precipitant concentrations, detection techniques, such as optical microscopy, light scattering, ultraviolet-visible (UV-vis) spectrophotometry, and refractive index, have play an essential role to observe the precipitated micrometer-sized particles (Simanzhenkov *et al.*, 2003). Micrometer-sized particles that have the appearance of 0.5  $\mu\text{m}$  are the onset of asphaltene precipitation. Maqbool *et al.* (2009) investigated kinetics of precipitation of crude oil-heptane mixture containing 50 vol % heptane and 50 vol % K-1 crude oil using microscopy. From micrographs, they revealed that at  $t = 0$  and 0.5 h, there were no precipitates to be observed. Around  $t = 0.9$  h, some haze (0.2-0.3  $\mu\text{m}$  particles) is present, and  $t = 1.4$  there were 0.5  $\mu\text{m}$  particles. At  $t = 2.5$  and 20 h, the was increasing in size of the particles to be 2-3  $\mu\text{m}$  as shown in Figure 2.5.



**Figure 2.5** Micrographs showing the time dependence of asphaltene precipitation for mixture containing 50 vol% heptane and 50 vol% K-1 crude oil (Maqbool *et al.*, 2009).

Aggregation has also been investigated depending on temperature (Buckley *et al.*, 2012). As can be seen in Figure 2.6 (a) and 2.6 (b), asphaltene particles join together to make chain-like structures. At higher temperature, the process is slightly faster and less asphaltenes separated from the oil.



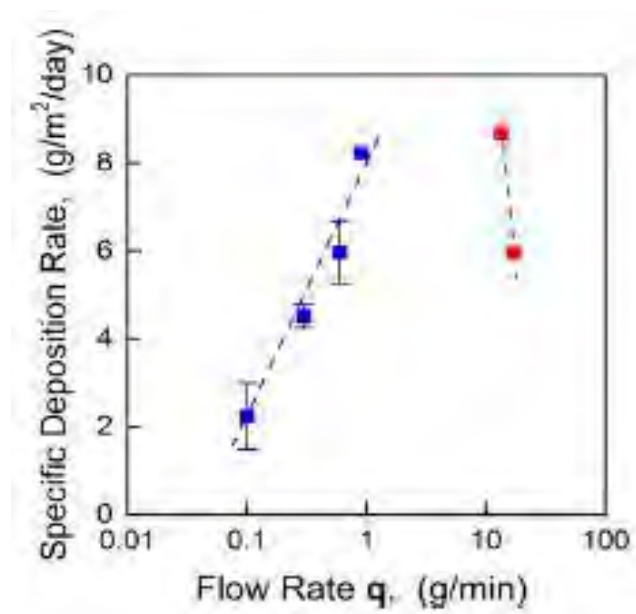
**Figure 2.6** Micrographs showing asphaltene aggregates in Oil B mixed with n-C7 (75:25) and aged at 25 (a) and 70 °C (b) (Buckley *et al.*, 2012).

## 2.4 Asphaltene Deposition

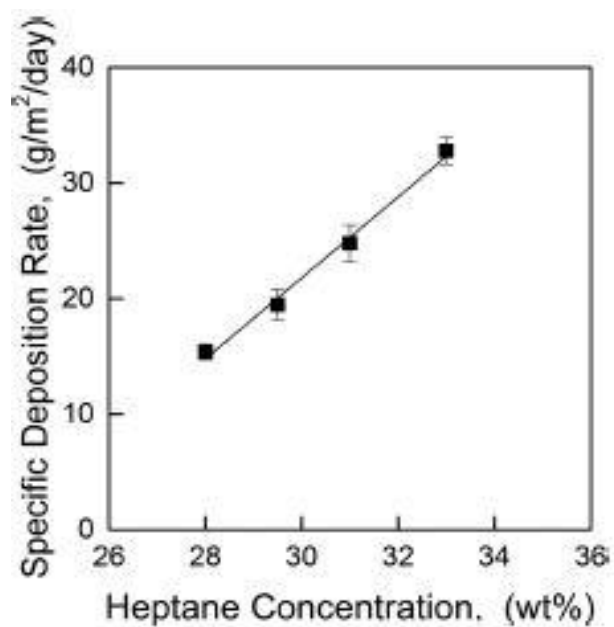
Destabilized asphaltenes can aggregate and deposit on the surface. Understanding in mechanisms of asphaltene deposition is desired. Published studies below are involving to asphaltene deposition in this work.

Vilas Bôas Fávero *et al.* (2016) studied mechanistic investigation of asphaltene deposition. Packed bed columns were introduced to their studies. A glass column was packed with 3 and 4 mm stainless steel beads, the packing was 13.2 cm long. Firstly, asphaltenes in crude oil were destabilized by adding heptane as precipitant. Secondly, the oil-heptane mixture reservoir was placed on a stir plate and pumped by peristaltic pump up through the column at a certain flow rate and run time. The deposit along the packing could be measured and characterized after the deposit have been collected by flowing chloroform into the column and dried the collected material until the mass was constant. They used a mass-transfer limited deposition model to predict asphaltene deposition rate along with experimental results. The model successfully explain the asphaltene deposition of nanometer-sized unstable asphaltenes in low flow rate regime shown in Figure 2.7 in blue where as in high flow rate regime, in red, cannot be explained by the model. In addition, they found out that increasing in heptane concentration results in a increase of specific deposition rate due to increasing of concentration of unstable asphaltenes shown in Figure 2.8 and 2.9.

Extensively, a relationship between specific deposition rate and concentration of unstable asphaltenes has been established. The specific deposition rate goes up while raising the concentration of unstable asphaltenes, noticed that the rate will be negative when the concentration is reaching zero, as shown in Figure 2.10.

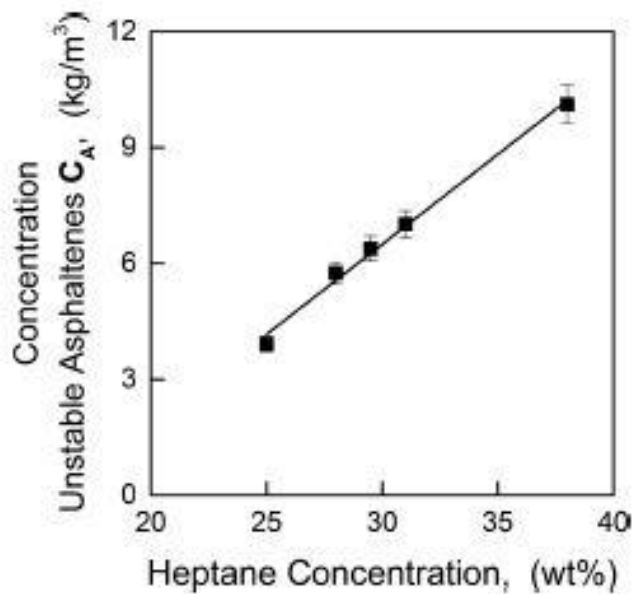


**Figure 2.7** Asphaltene deposition rate as a function of the fluid flow rate for 67% heptane in Oil E (Vilas Bôas Fávero *et al.*, 2016).

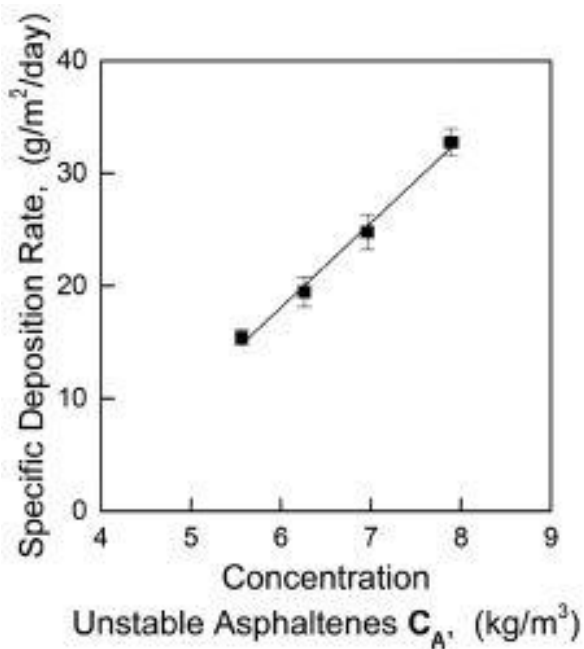


**Figure 2.8** Asphaltene deposition rate as a function of heptane concentration in Oil C (Vilas Bôas Fávero *et al.*, 2016).



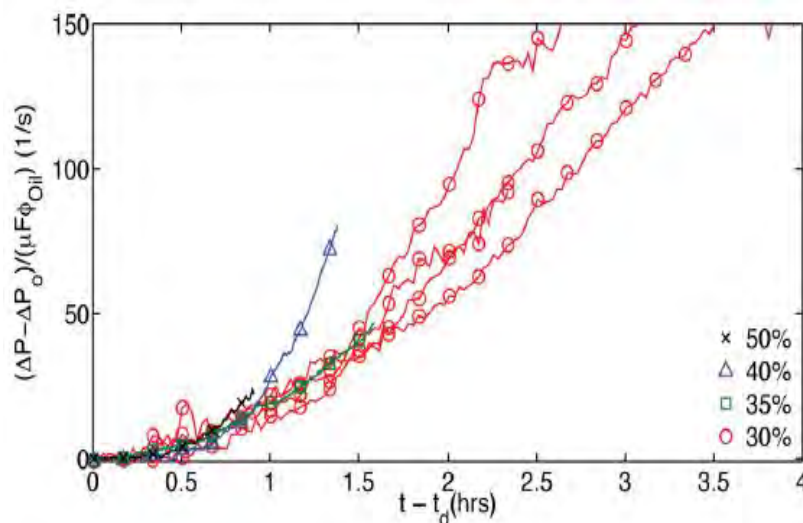


**Figure 2.9** Concentration of unstable asphaltenes as a function of heptane concentration in Oil C (Vilas Bôas Fávero *et al.*, 2016).



**Figure 2.10** Asphaltene deposition rate as a function of heptane concentration of unstable asphaltenes in heptane-oil mixture (Vilas Bôas Fávero *et al.*, 2016).

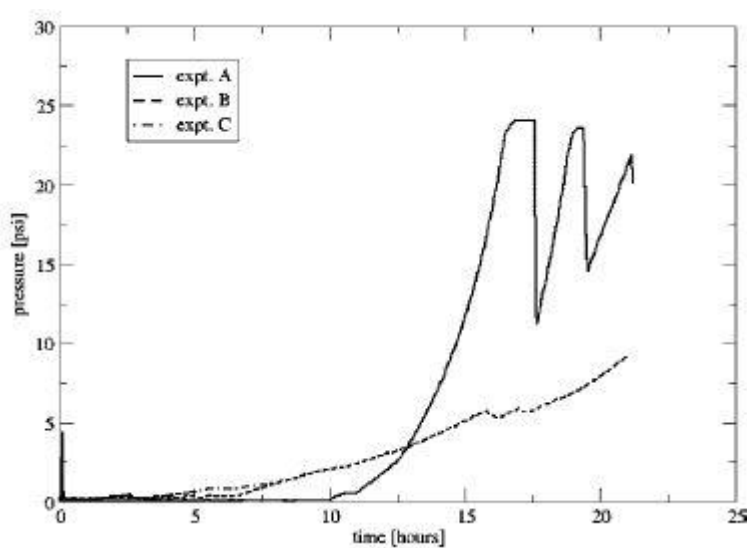
Hoepfnel *et al.* (2013) studied a fundamental study of asphaltene deposition. They investigated two crude oils, Oil A and WY Oil, which was Oil A has asphaltene content more than WY Oil. Heptane and oil were first separately flown into mixing capillary, then into deposition capillary, which had different diameters and lengths. Effluent was collected, and pressure drops between inlet and outlet of the capillary were monitored using differential pressure transducer. They also studied particle aging using the effluent from deposition. The effluent was diluted with heptane and continuously stirred for 95 h before being fed into another capillary using peristaltic pump. The results revealed that deposition happened even though asphaltene aggregates are submicrometer, meaning that the deposition of asphaltene aggregates is independent on the instantaneous onset point. The deposition also happened at low concentrations of heptane, but required long time to detect. Moreover, they found out that the deposit profile was nonuniform, where the inlet of the capillary was thicker than outlet, being confirmed by SEM images. From deposition of precipitated and aged asphaltenes experiments, demonstrating that asphaltenes only deposit when they are in the process of aggregating and that aged asphaltenes aggregates do not deposit. The normalization results illustrated that the pressure drop profiles for different heptane concentrations roughly collapsed to a single curve; however, at 40 and 50 vol.% heptane experiments began to deviate from the normalized behavior once the pressure drop increased significantly as shown in Figure 2.11.



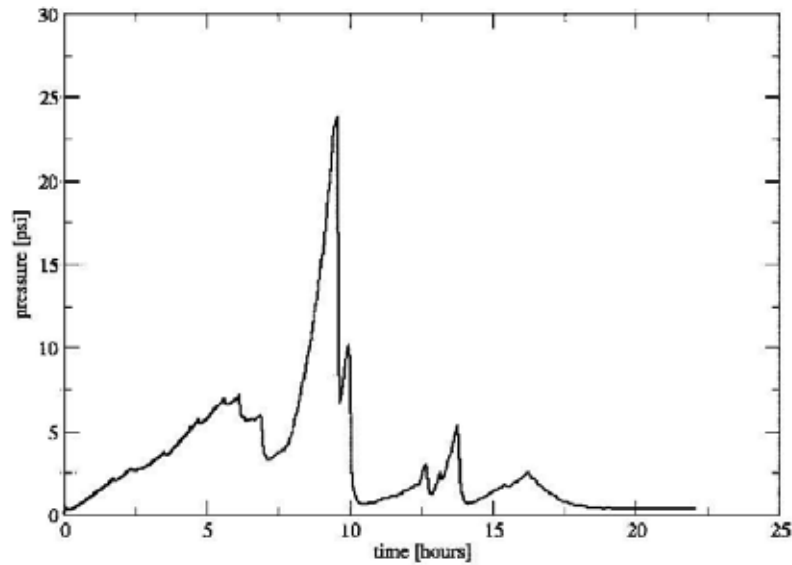
**Figure 2.11** Normalized deposition pressure drop profiles for heptane in Oil A (Hoepfnel *et al.*,2013).

Boek *et al.* (2008) studied deposition of colloidal asphaltene in capillary flow: experiments and mesoscopic simulation. They used a rectangular glass microcapillary, which was 100 mm long, 600  $\mu\text{m}$  wide and 150  $\mu\text{m}$  deep. The capillary wall thickness was 50  $\mu\text{m}$ , giving a slot dimension of 500  $\times$  50  $\mu\text{m}$  and a capillary volume of 2.5  $\mu\text{L}$ . The model fluid system comprising of asphaltenes being extracted from Cold Lake crude oil and mixed with toluene at concentration 1  $\text{g L}^{-1}$  was used in this experimental work. They have investigated the effect of flow rates, at 5  $\mu\text{L min}^{-1}$  and 10  $\mu\text{L min}^{-1}$  of heptane and the model fluid system at a 60:40 ratio. The results revealed that for a constant flow rate of 5  $\mu\text{L min}^{-1}$  for three repeat experiments, the early time behavior showed a slow increase in the pressure drop, due to the continuous deposition of asphaltenes. For later time, the slopes of these curves, the rate of asphaltene deposition, were different. In experiment A, a maximum pressure of 24 psi was reached, followed by a series of pressure cycles as can be seen in Figure 2.12. This behavior corresponds to increased asphaltene retention and asphaltene deposition-erosion/entrainment cycles, which was confirmed by micrographs of asphaltene retention as a function of time for experiment A. At constant flow rate of 10  $\mu\text{L min}^{-1}$ , the pressure increased at rate of 1.15  $\text{psi h}^{-1}$ , which is more than that at previous condition. After 8.5 h the pressure went up moderately to the maximum point of 12.5  $\text{psi h}^{-1}$ . It dropped down and built

up at the time of 9.5 h, then followed by the fast decrease in pressure as shown in Figure 2.13. The sharply increase and decrease of the pressure were explained that at higher shear rate, because of higher flow rate, the asphaltenes have a higher collision frequency and therefore an increased likelihood to aggregate, leading to more deposit, after that the deposit is entrained by the shear force.

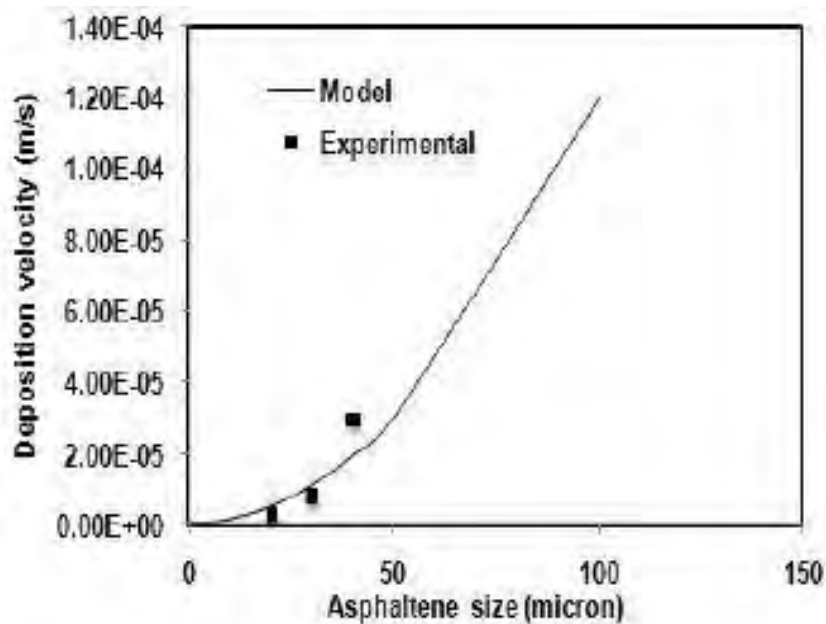


**Figure 2.12** Pressure drop history for a constant flow rate of  $5 \mu\text{L min}^{-1}$  for three repeat experiments (Boek *et al.*, 2008).

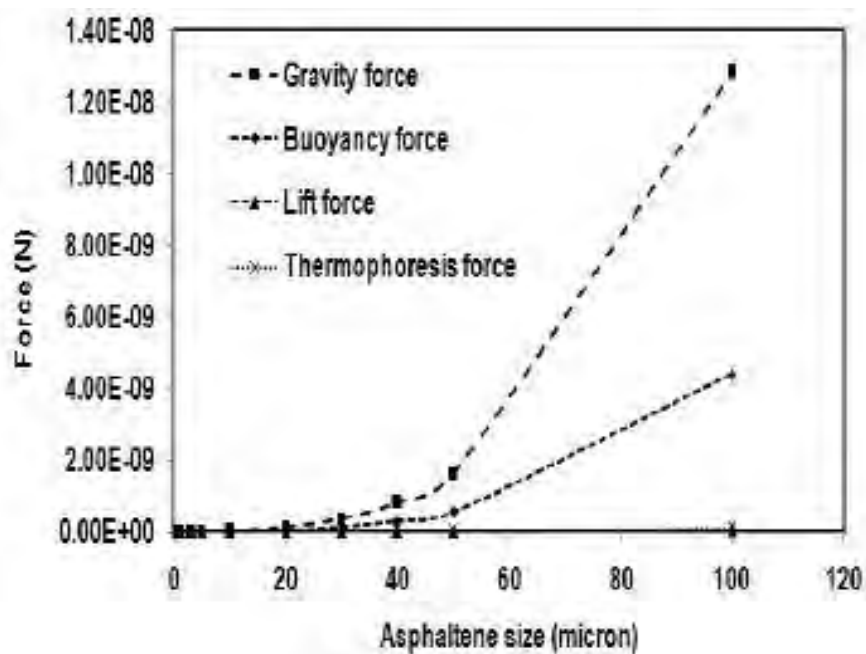


**Figure 2.13** Pressure profile for the higher flow rate of  $10 \mu\text{L min}^{-1}$  (Boek *et al.*, 2008).

Behruz *et al.* (2013) studied modeling of asphaltene deposition in pipelines. Their model included shear induced lift force, thermophoresis, drag force, and buoyancy force. According to their modeling results along with aerosols deposition data, they have found out that there is an increase of deposition velocity with increasing of asphaltene particle size, which is in a good agreement with the aerosols deposition data shown in Figure 2.14. Furthermore, the gravitational force is the most influenced by a change of asphaltene particle size as shown in Figure 2.15.

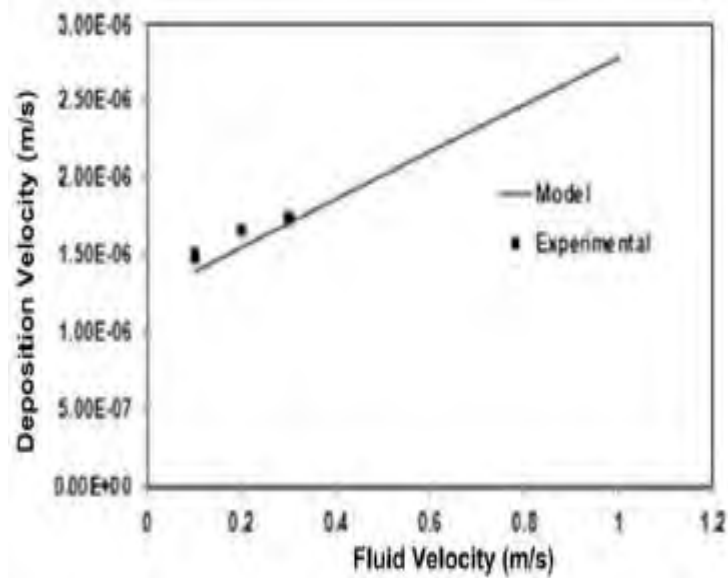


**Figure 2.14** Effect of asphaltene particle size on deposition velocity (Behruz *et al.*, 2013).



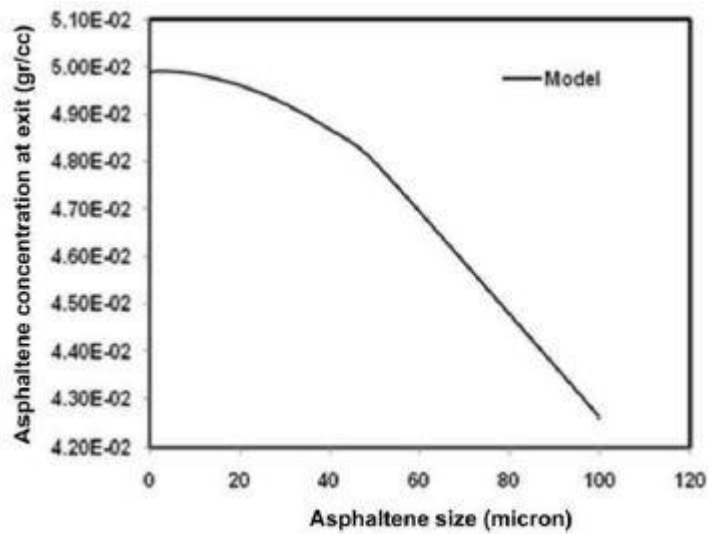
**Figure 2.15** Effect of asphaltene particle size on gravitaional force, buoyancy foice, lift force, and thermophoresis force (Behruz *et al.*, 2013).

Effect of fluid velocity on deposition velocity has also been investigated. The deposition velocity predicted using the model grows up with the fluid velocity increment and the trend from the model is in the same way as the data given by experimental results as shown in Figure 2.16.

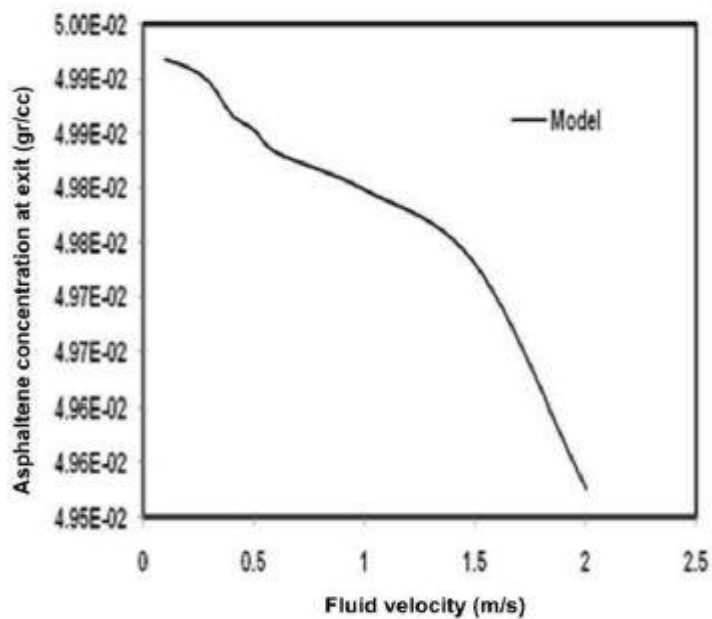


**Figure 2.16** Effect of fluid velocity on deposition velocity (Behruz *et al.*, 2013).

More importantly, relationships of asphaltene particle size and fluid velocity with asphaltene concentration at exit pipe have been modeled. The results showed that the asphaltene concentration drops down while the asphaltene particle size and the fluid velocity go up as shown in Figures 2.17 and 2.18.



**Figure 2.17** Effect of asphaltene particle size on asphaltene concentration at pipe exit (Behruz *et al.*, 2013).

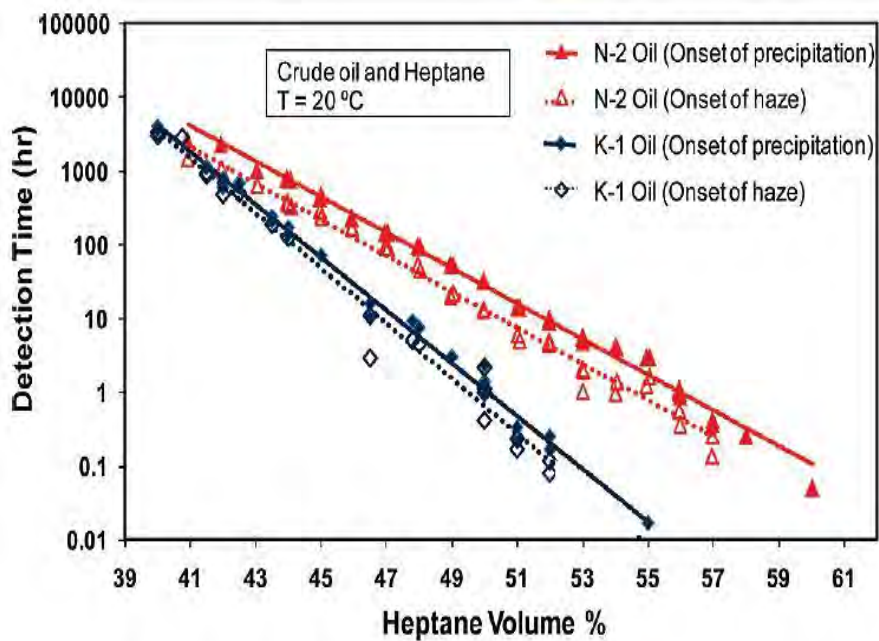


**Figure 2.18** Effect of fluid velocity on asphaltene concentration at pipe exit (Behruz *et al.*, 2013).

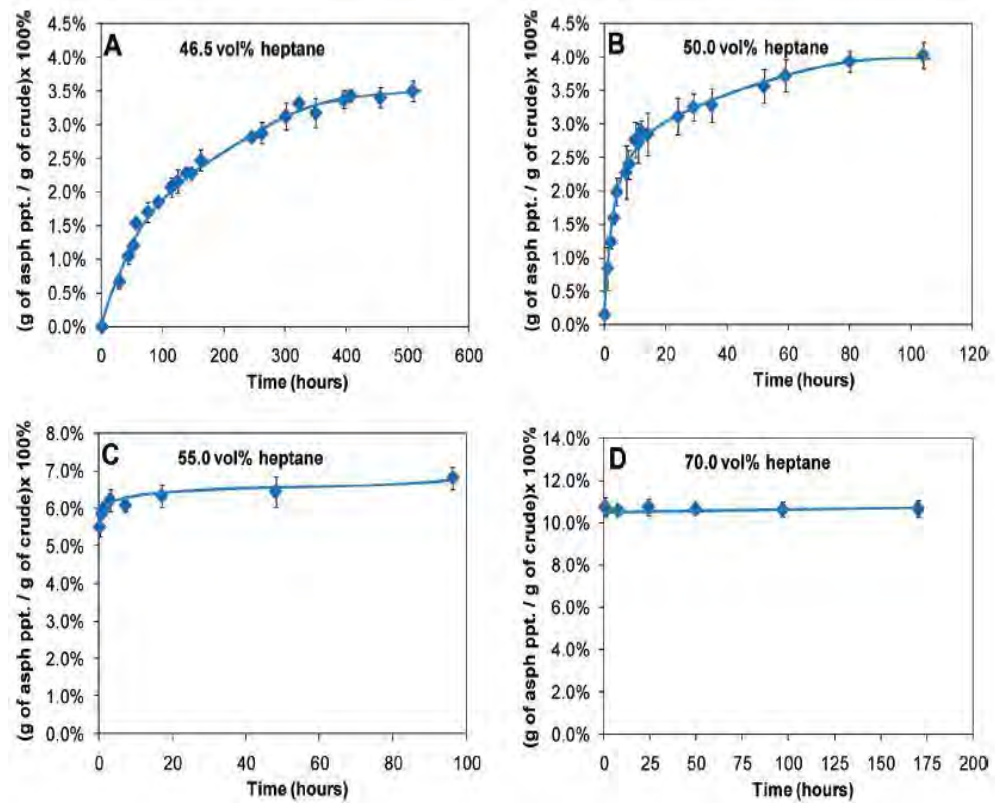


## 2.5 Concentration of Unstable Asphaltenes in Aged Oil-Heptane Mixture

Kinetics of unstable asphaltenes has been studied by Maqbool *et al.* (2009) using centrifugation of aged oil-heptane mixtures at various heptane concentrations and crude oils. Detection time technique was introduced to support the centrifugation technique. For example, K-1 and N-2 crude oils mixed with different heptane concentrations were detected using a microscopy to observe onset of haze and precipitated asphaltene. Thereafter, the detection times for onset of precipitation and onset of haze for varying heptane concentrations were constructed as shown in Figure 2.19. Herein, the K-1 crude oil has instantaneous asphaltene precipitation at 55 vol % is illustrated for centrifugation technique. In Figure 2.20 (A), At 46.5 vol % heptane below the instantaneous point, the mass concentration of precipitated asphaltene gradually increases over time and eventually reaches a plateau value. For the concentration higher than 46.5 vol%, the plateau value shifts to higher in height as shown in Figure 2.10 B, C, and D. As can be observed in the plots, the plateau values of precipitated asphaltenes at precipitant concentrations well above the instantaneous precipitation can be measured in very short time, meaning that the kinetics of precipitation occurs very fast. On the other hand, the kinetics is very slow at precipitant concentrations well below the instantaneous precipitation, it possibly takes months or even years to reach plateau value.



**Figure 2.19** Detection times for onset of precipitation and onset of haze for varying heptane concentrations using K-1 and N-2 crude oils (Maqbool *et al.*, 2009).



**Figure 2.20** Amount of asphaltenes precipitated as a function of time for K-1 crude oil for varying heptane content: (A) 46.5 vol % heptane, (B) 50.0 vol % heptane, (C) 55.0 vol % heptane, and (D) 70.0 vol % heptane (Maqbool *et al.*, 2009).

## **CHAPTER III**

### **METHODOLOGY**

#### **3.1 Materials**

##### 3.1.1 Crude Oils

Erin and Harry crude oils were provided by the sponsors of the University of Michigan industrial affiliates program and used to perform detection time, centrifugation, and asphaltene deposition experiments.

##### 3.1.2 Solvent

HPLC grade n-heptane from Fisher was used as precipitant to destabilize asphaltenes in crude oils for all the experiments and to wash cakes during centrifugation experiments. Density and viscosity at room temperature (20°C) are 683 kg/m<sup>3</sup> and 0.4 mPa·s, respectively.

HPLC grade chloroform containing 0.75% ethanol as preservative was used to be a solvent to collect the deposit in the packed bed column and to clean the column after the experiments were finished. Density is 1480 kg/m<sup>3</sup> and viscosity is 0.56 mPa·s at 20°C.

#### **3.2 Equipment:**

##### 3.2.1 Stainless Steel Spheres

Stainless steel spheres type 316 2 mm in diameter from New England Miniature Ball, 3-mm in diameter from Goodfellow Cambridge, and 4-mm in diameter from Alfa Aesar were used to pack in the glass column. The composition was shown in Table 3.1.

**Table 3.1** Composition of stainless steel sphere

Element	Percent by weight
Iron (Fe)	67.5
Chromium (Cr)	17
Nickel (Ni)	13
Molybdenum (Mo)	12.5

### 3.2.2 Packed Bed Column

Glass column with 10 mm inner diameter and 900 mm in length, complete with adjustable plungers at the top & bottom, with PTFE seals from Ace Glass Incorporated was used as packed bed column.

### 3.2.3 Peristaltic Pump

Masterflex Peristaltic Pump comprising of two main parts: Masterflex L/S Digital Pump Drive, EW-07522-20 and Masterflex L/S Easy-Load from Cole-Parmer Instrument Company, was used to add heptane to crude oil, to pump the oil-heptane mixture into packed-bed column, and to flow chloroform to collect deposited material along the packed bed column.

### 3.2.4 Cover Glass

25x25 mm and 18x18 mm glass plates were used in detection time experiment. After a droplet of sample was withdrawn, it was quickly placed on the bigger glass plate then followed by the smaller one on top. Then, the sample was put under a microscope.

### 3.2.5 Optical Microscope

Nikon with model Eclipse E600 with 50×objective lens and 10×eyepiece equipped with Nikon DS-Fi2 camera head and Nikon DS-U3 digital camera was used to observe aggregated asphaltenes in samples of oil-heptane mixture. The smallest size at which can be detected under microscope is 500

nanometers. The microscope was connected to computer in such a way that photos of the aggregated asphaltenes can be taken and recorded by using NIS-Elements program.

### 3.2.6 Analytical Balance

Mettler Toledo MS3002S New Classic Precision Balance with 3200 g maximum capacity, 0.02 g linearity deviation, and 0.01 g readability was used to weigh the mass of flasks, crude oil-heptane mixture during the mixture preparation step. In addition, it was used to weigh the centrifuge tube during the crude oil pretreatment step.

Mettler Toledo XS204 Excellence XS Analytical Balance with 220 g maximum capacity, 0.0002 g linearity deviation, and 0.0001 g readability was used to weigh the microcentrifuge tube during asphaltene quantification step. It was also used to weigh vial containing the mass of collected material obtained from asphaltene deposition experiment.

### 3.2.7 Vacuum Oven

Thermo Fisher Scientific Linberg/Blue M™ vacuum oven equipped with 2047 DryFast Diaphragm Pump was used to evaporate chloroform out of the vial containing mass of collected material. The temperature was set at 70 °C.

### 3.2.8 Incubator

Fisher Scientific Isotemp Incubator Model 637D was used to evaporate heptane out of the microcentrifuge tube containing asphaltenes and remaining heptane.

### 3.2.9 Centrifuge

Thermo Scientific™ Sorvall™ Legend™ X1 centrifuge equipped with Fiberlite™ F15-8 x 50cy Fixed Angle rotor was used to centrifuge crude oil during the crude oil pretreatment step and reservoir of oil-heptane mixture before feeding into packed bed column and doing detection time experiment.

Eppendorf 541R microcentrifuge with 1400 rpm maximum rotational speed was used to centrifuge 1.5 ml microcentrifuge tube containing crude oil-heptane mixture.

#### 3.2.10 Sonicator

Branson 5510 ultrasonic bath was used to vibrate the asphaltene-heptane mixture in microcentrifuge tube to make it well-homogenized during asphaltene quantification step.

#### 3.2.11 Stir Plate

CORNING PC-410D stir plate was used to keep the crude oil-heptane mixture well-homogenized when the mixture was prepared.

CORNING PC-353 stir plates were used to keep the crude oil-heptane mixture well-homogenized during asphaltene deposition experiments.

RO 10 power IKAMAG® stir plate was used to keep the crude oil-heptane mixture well-homogenized when performing centrifugation and detection time experiments.

#### 3.2.12 Propeller

Propeller connected with the electrical motor was used to homogenize crude oil prior to inserting in the centrifuge to separate solid particles out in crude oil pretreatment.

#### 3.2.13 Vial

1 dram clear 15x45 vial with PTFE lined cap from Scientific Specialities was used to keep the crude oil-heptane mixture during detection time experiment.

8 dram clear 25x95 vial with PTFE lined cap from Glass Vials was used to collect the collected material from deposition experiment.

#### 3.2.14 Connector and Tubing

Teflon tubing with 1.5 mm inner diameter and 0.3 mm wall thickness, from Ace Glass Incorporated and Master flex Viton tubing, L/S13 with 0.8 mm inner diameter were used to connect peristaltic pump and packed bed column.

U-145 Stainless steel capillary tube with 1/16 inch inner diameter and U-146 Stainless steel capillary tube with 1/16 inch inner diameter were used as connectors to connect the whole parts together.

### 3.3 Software

#### 3.3.1 Microsoft Excel

#### 3.3.2 NIS-elements

### 3.4 Methodology

#### 3.4.1 Crude Oil Pretreatment

Crude oils delivered from Nalco Company were homogenized by vigorously shaking and was stirred for 3 hours. Thereafter, it was transferred to 50 mL centrifuge tubes and was centrifuged at rotational speed of 14000 rpm for 3 hours to remove sands, wax, water, etc. Eventually, supernatant was poured into amber bottles with label.

#### 3.4.2 Detection Time of Oil-Heptane Mixture for Deposition Experiment

Before starting asphaltene deposition experiments, heptane concentrations were selected by performing detection time experiments for various heptane concentrations to determine the frequency of changing reservoir to avoid large asphaltene particles, not larger than 500 nm, during deposition experiment.

A certain amount of crude oil was prepared in 25 ml Erlenmeyer flask. Then, desired amount of heptane was started adding into the prepared crude oil at flow rate 1mL/min using the peristaltic pump while the oil-heptane mixture was kept stirred. After desired heptane concentration-oil mixture was obtained, the mixture



was sealed and let stir. A drop of the mixture was withdrawn over time and placed under optical microscope. The time that particles are started observing is defined as detection time. Finally, the concentrations at which asphaltene deposition could be performed are based on detection time curves and images.

### 3.4.3 Centrifugation experiment

#### *3.4.3.1 Centrifugation of Aged Oil-Heptane Mixture*

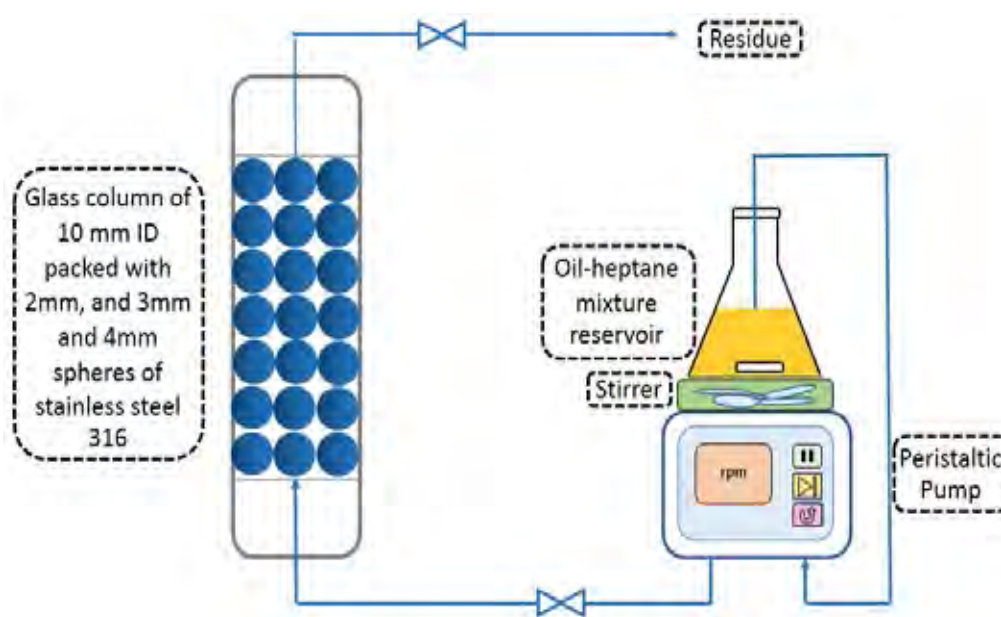
A desired amount of crude oil-heptane mixture was prepared in 125 mL Erlenmeyer flask at a given heptane concentration, then, desired amount of heptane was started adding into the prepared crude oil at flow rate 3mL/min using the peristaltic pump while the oil-heptane mixture was kept stirred. After desired heptane concentration was accomplished, the mixture was sealed and stirred all the time. Three samples of 1.5 mL from each mixture were withdrawn from Erlenmeyer flask, transferred to 1.5 mL microcentrifuge tube, and centrifuged at 14,000 rpm for 10 minutes. Thereafter, the cake containing precipitated asphaltenes was sonicated and washed several times with heptane until the color of supernatant is identical to the previous supernatant. After that, the cake was dried in the incubator at 70 °C for three days, and weighed. The experiment was performed continuously over and over again for a period of time until the concentration of unstable asphaltenes was supposed to reach a plateau value.

#### *3.4.3.1 Centrifugation of Fresh Oil-Heptane Mixture*

A desired amount of crude oil-heptane mixture was prepared in 125 mL Erlenmeyer flask at a given heptane concentration, then, desired amount of heptane was started adding into the prepared crude oil at flow rate 3mL/min using the peristaltic pump while the oil-heptane mixture was kept stirred. After desired heptane concentration was accomplished. Next, the oil-heptane mixture was immediately transferred to 50 mL centrifuged tubes and centrifuged for a desired time, in this study, 10, 30, 50, and 300 minutes. Afterwards, the supernatant was further used as reservoir for asphaltene deposition experiment and the cakes were proceed the same procedure as the cakes obtained from centrifugation of aged oil-heptane mixture.

### 3.4.4 Asphaltene Deposition

The asphaltene deposition apparatus consisted of a glass column with an ID of 10 mm packed with 2mm, and 3 mm and 4 mm of stainless steel spheres until the total length of the packed bed column was 13.2 cm. The column was connected to peristaltic pump and reservoir containing the mixture of crude oil and heptane using Teflon tubes and vitons. The schematic of apparatus is shown in Figure 3.1.



**Figure 3.1** Schematic of asphaltene deposition apparatus.

The liquid from reservoir was introduced into the packed bed using peristaltic pump at a desired flow rate for a period of time. Mass flow rate was measured occasionally and pump rpm was adjusted if necessary to ensure the flow rate was constant. After running the mixture of oil-heptane through the column for the desired time, the flow was stopped. Then, the pump was reversed direction and set to be 1 rpm to drain the liquid inside the bed. Chloroform was then fed into the column to collect the deposited material. The effluent chloroform plus deposited material was collected in a vial and let dry in a fume hood overnight before putting in a vacuum oven. The dry mass obtained was referred to as mass of collected material for that run condition. Chloroform was flown for extra 10 minutes to completely

clean all the spheres and column. Afterwards, packed bed was dried by flowing air. The dry mass would be plotted as a function of run time to further calculate rate of deposition.

## CHAPTER IV

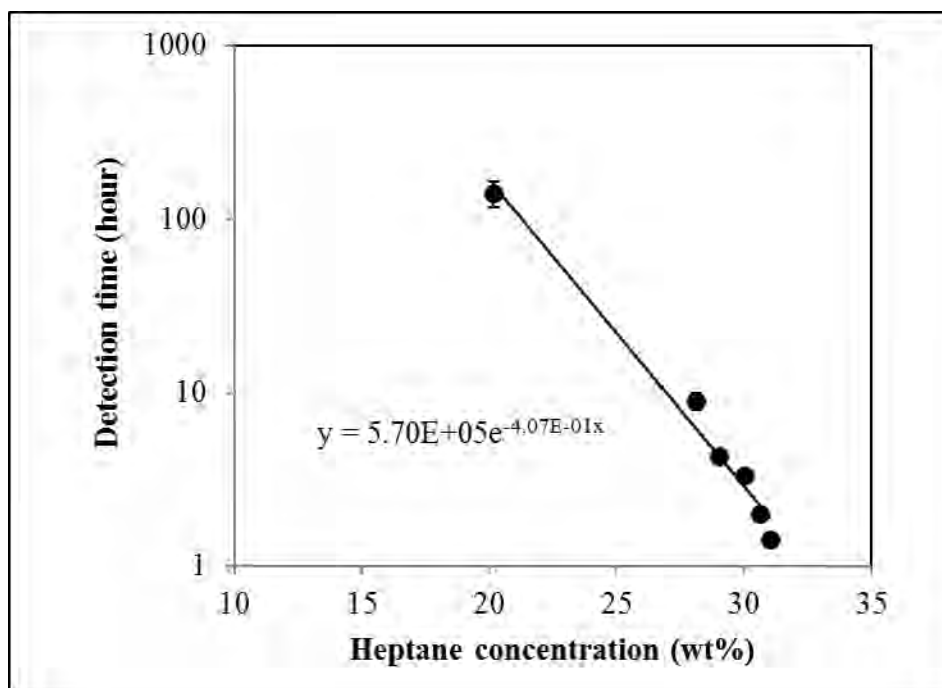
### RESULTS AND DISCUSSION

#### 4.1 Selection of Heptane wt% to be Used in Asphaltene Deposition Experiment

To destabilize asphaltenes in crude oil, heptane was added into Harry crude oil. A sample of oil-heptane mixture at a given concentration was withdrawn and placed under microscope. The time that it starts observing asphaltene particles is called detection time. The smallest size of particles visible under the microscope is about 500 nm. Results of the detection time experiment for Harry crude oil are shown in Table 4.1. As heptane concentration increases, detection time decreases. It means that heptane concentration increases, unstable asphaltenes are more quickly detected by microscope. The data in Table 4.1 is plot in semi-log scale, which is shown in Figure 4.1. As seen in Figure 4.1 the detection time increases exponentially with decreasing heptane concentration. The heptane concentration that was picked up as an operation concentration was 30.5 wt%. During the deposition run, reservoir was replaced every two hours to avoid large particles and settle down of those large particles by gravity.

**Table 4.1** Detection time results of Harry crude oil

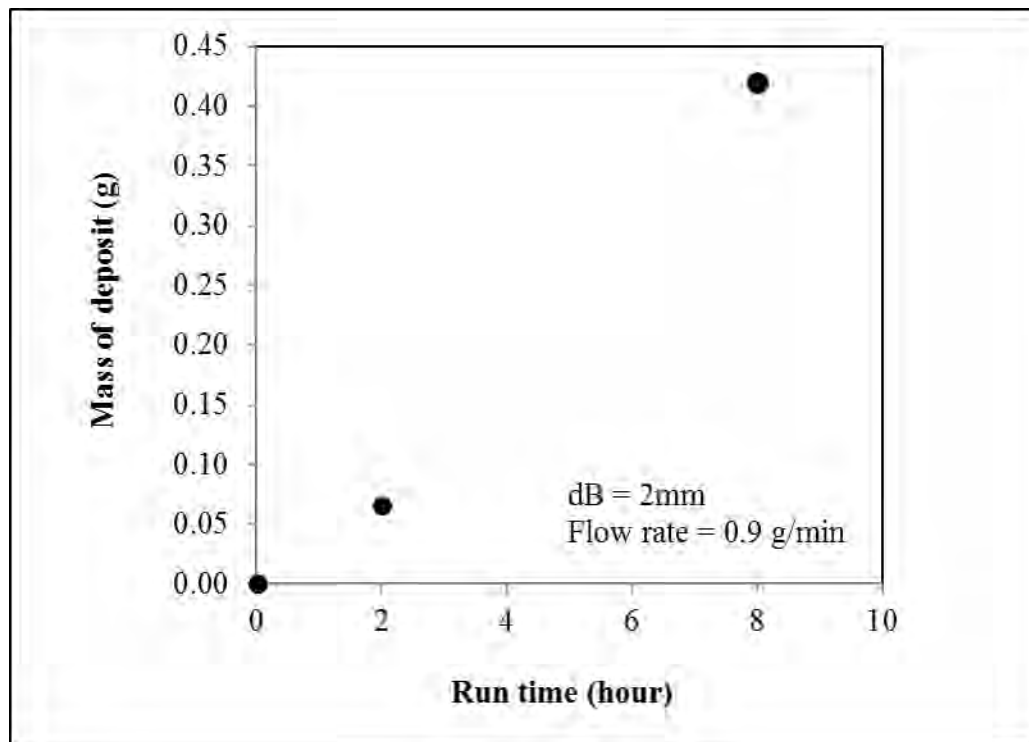
Heptane Concentration (wt%)	Detection Time (hour)
28	9
29	4.3
30	3.2
30.5	2
31	1.4



**Figure 4.1** Detection time results of Erin crude oil.

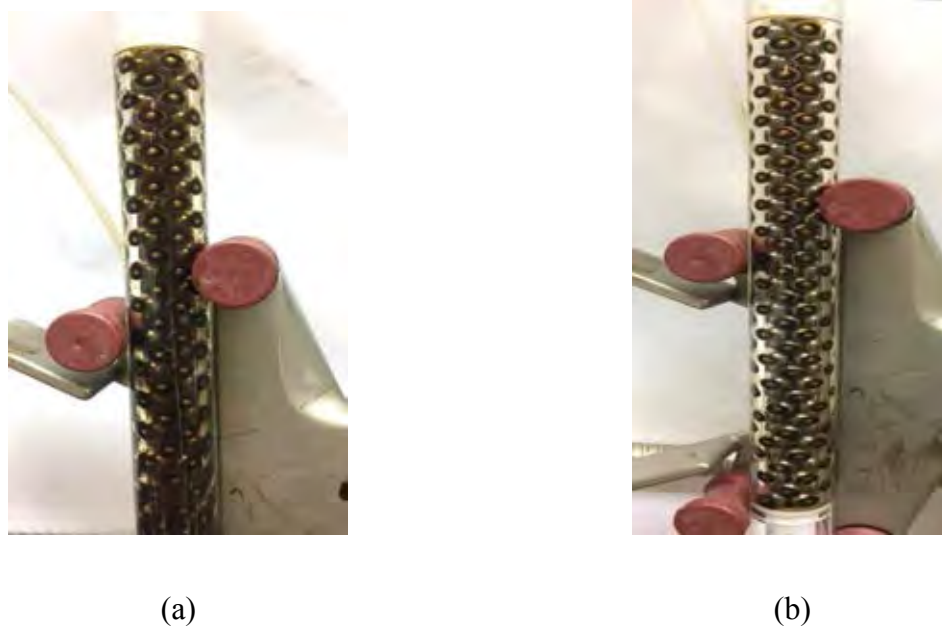
## 4.2 Asphaltene Deposition Experiment

In this asphaltene deposition experiment, it was divided into two effects. The first is effect of bead size on asphaltene deposition. The second is effect of concentration of unstable asphaltenes on asphaltene deposition rate. Before performing experiments with the two effects, appropriate run time and flow rate were chosen. As shown in Figure 4.2, mass of deposit at various run times, which are 2 and 8 hours. The experiment was performed with packed bed packed with 2 mm beads. Mass of deposit linearly increases as run time increases. Since mass of deposit at 2 hr is significantly less than mass of deposit at 8 hr. In order to further characterize and analyze the mass of deposit obtained from experiment, asphaltene deposition experiments were performed for 8 hours and at flow rate 0.9 g/min.



**Figure 4.2** Mass of deposit as a function of run time.

To measure actual mass of deposit, 1 min-run experiments are needed. 1 min-run experiment was performed to measure amount of trapped liquid between bead and bead, and between bead and wall of column in packed bed as shown in Figure 4.3 (b). After running deposition experiment for 8 hours, all material in column was collected. The material consisted of deposit and trapped liquid as shown in Figure 4.3 (a). Eventually, mass of deposit was calculated by subtracting the mass of collected material to mass of trapped liquid.

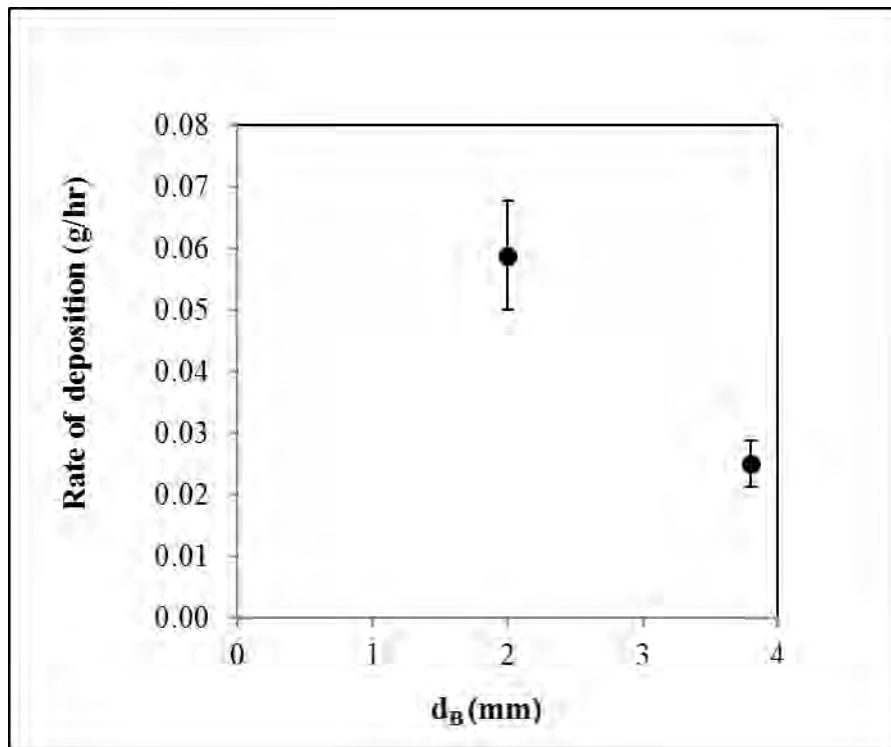


**Figure 4.3** All material that deposited on surface of beads (a), Liquid trapped (b).

### 4.3 Effect of Bead Size on Asphaltene Deposition

To study effect of bead size on asphaltene deposition, various bead sizes have been used such as 0.8, 1, 2, and 3 and 4mm packed together or 3.8mm. There was a problem with draining due to tension force of oil-heptane mixture when packed bed was packed with 0.8 and 1mm bead size. After 8 hour experiment was stopped, liquid in column was slightly drained out of column, but there was some liquid still remained at the bottom of the column could not be drained properly as shown in Figure 4.3 (a) and (b). Therefore, the minimum bead size that can be used for asphaltene deposition experiment is 2 mm. For further experiments, result from 2 and 3.8mm are going to be compared.

Figure 4.4 shows rate of deposition as a function of bead diameter. Rate of deposit decreases from 0.06 to 0.025 g/hr as bead diameter increases from 2 to 3.8mm.



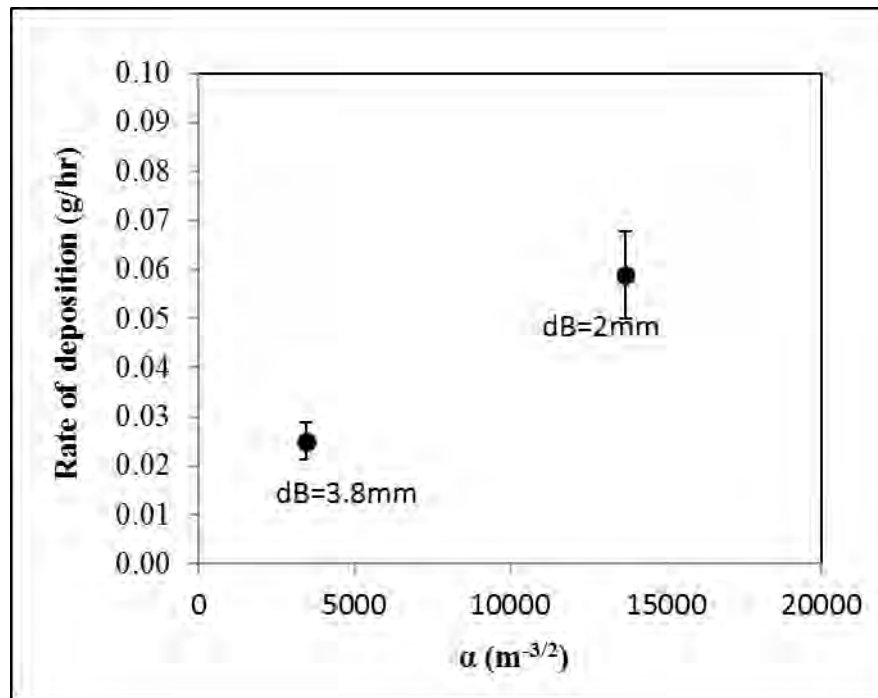
**Figure 4.4** Rate of deposition as a function of bead diameter.

From mass-transfer limited deposition model proposed by (Vilas Bôas Fávero *et al.*, 2016), equation (4.1), Deposition rate is not just only a function with diameter of bead, but it is also a function of porosity of packed bed,  $\phi$ .

$$\text{Deposition Rate} = \frac{6L(1-\phi)^{\frac{3}{2}}}{\phi} A_c^{\frac{1}{2}} d_B^{-\frac{3}{2}} \mu^{-\frac{1}{6}} \rho^{-\frac{1}{3}} C_{A0} D^{\frac{2}{3}} q^{\frac{1}{2}} \quad (4.1)$$

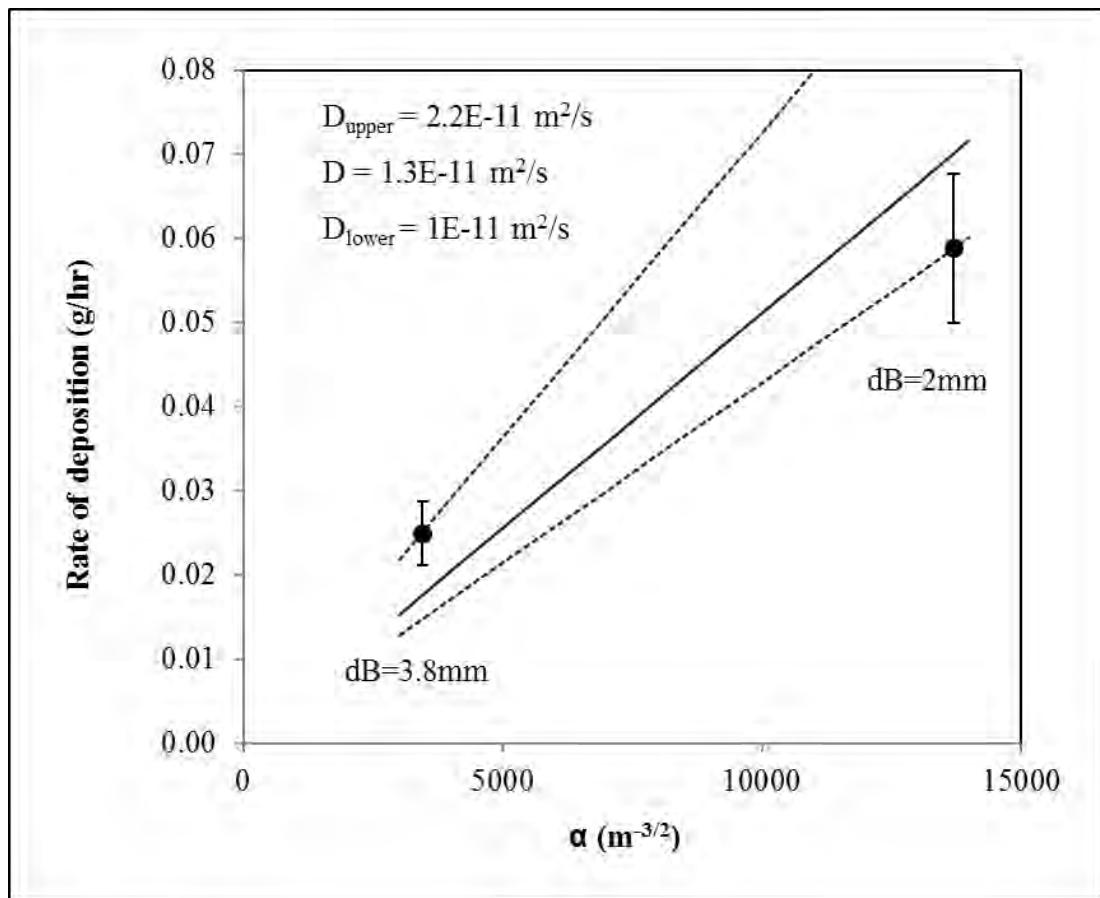
By defining the term  $\frac{(1-\phi)^{\frac{3}{2}}}{\phi} d_B^{-\frac{3}{2}}$  as an alpha ( $\alpha$ ), and then the rate of deposition from the experimental result is plot as a function of the  $\alpha$  as shown in Figure 4.5 below. As  $\alpha$  goes up, rate of deposition also goes up.





**Figure 4.5** Rate of deposition as a function of  $\alpha$ .

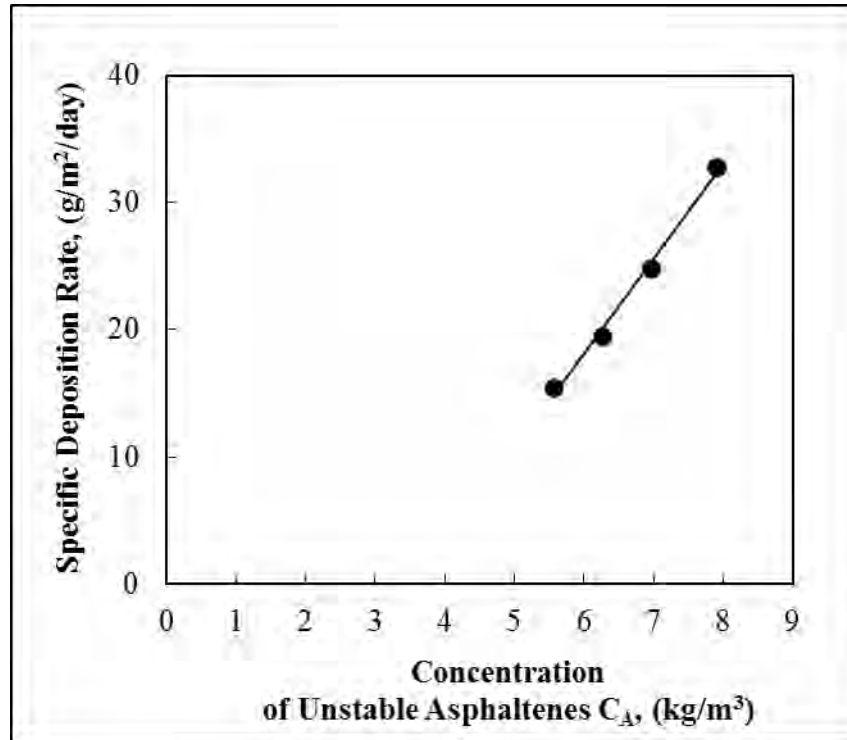
The rate of deposition can be predicted using equation (4.1) by plugging value of  $L$ ,  $AC$ ,  $\mu$ ,  $\rho$ ,  $CA_0$ , and  $q$  into the equation and varying  $\alpha$ . Finally, upper value, appropriate value, and lower value of diffusivity are obtained, which are  $2 \times 10^{-11}$ ,  $1.3 \times 10^{-11}$ , and  $1.0 \times 10^{-11} \text{ m}^2/\text{s}$ , respectively as shown in Figure 4.6 given by the model.



**Figure 4.6** Rate of deposition as a function of  $\alpha$  given by experiment and mass-transfer limited deposition model.

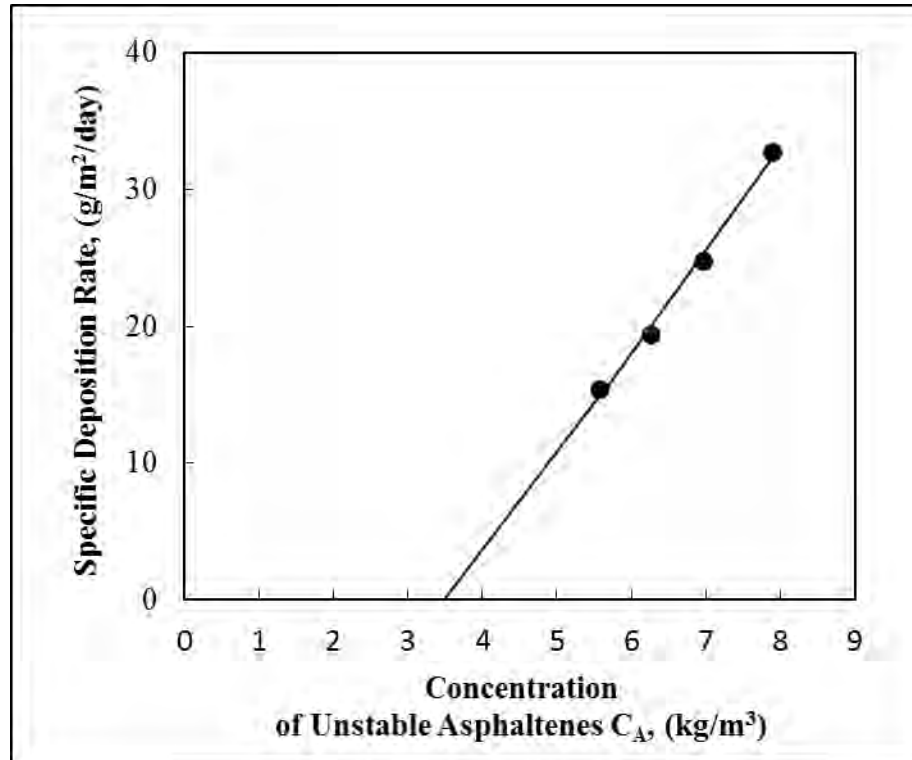
#### 4.4 Effect of Concentration of Unstable Asphaltenes on asphaltene deposition

Vilas Bôas Fávero *et al.* (2016) have studied specific deposition rate of deposition as a function of concentration of unstable asphaltenes as shown in Figure 4.7.



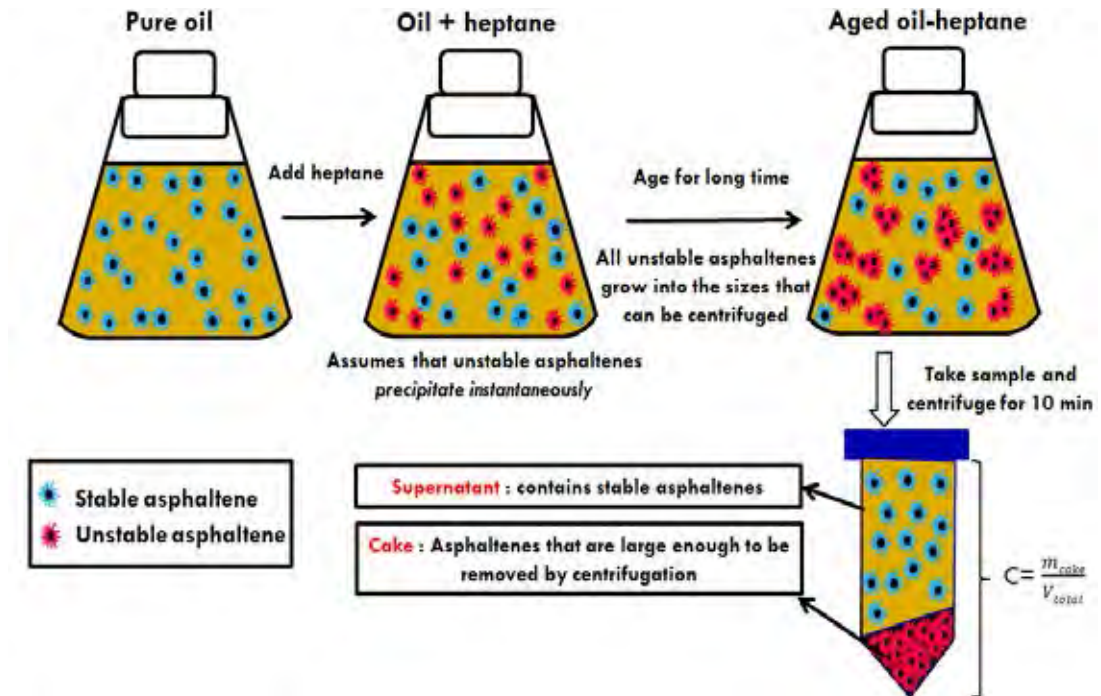
**Figure 4.7** Specific rate of deposition as a function of concentration of unstable asphaltenes (Vilas Bôas Fávero *et al.*, 2016).

In the plot, extrapolation of the line passed through the data predicts that the specific rate will be zero when the concentration of unstable asphaltenes will be approximately equal to 3.5 kg/m<sup>3</sup> as illustrated in Figure 4.8.



**Figure 4.8** Extrapolated data of specific rate of deposition as a function of concentration of unstable asphaltenes.

The concentration of unstable asphaltenes in this plot was measured from centrifugation of aged oil-heptane mixture method (Maqbool *et al.*, 2011) as illustrated in Figure 4.9.

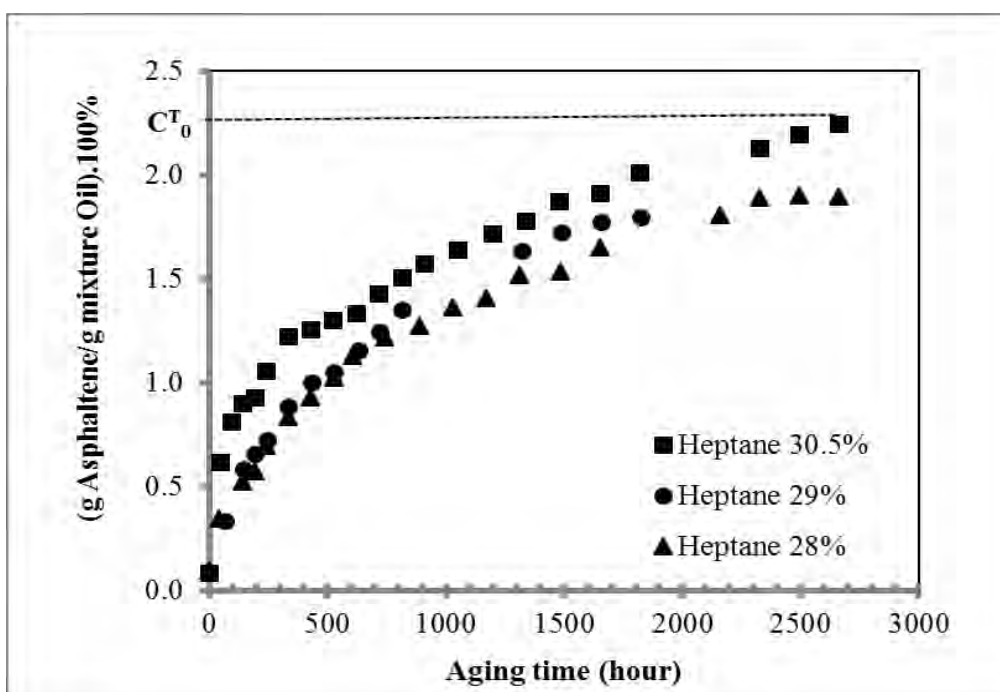


**Figure 4.9** Schematic illustrating the method measuring concentration of unstable asphaltenes of aged oil-heptane mixture.

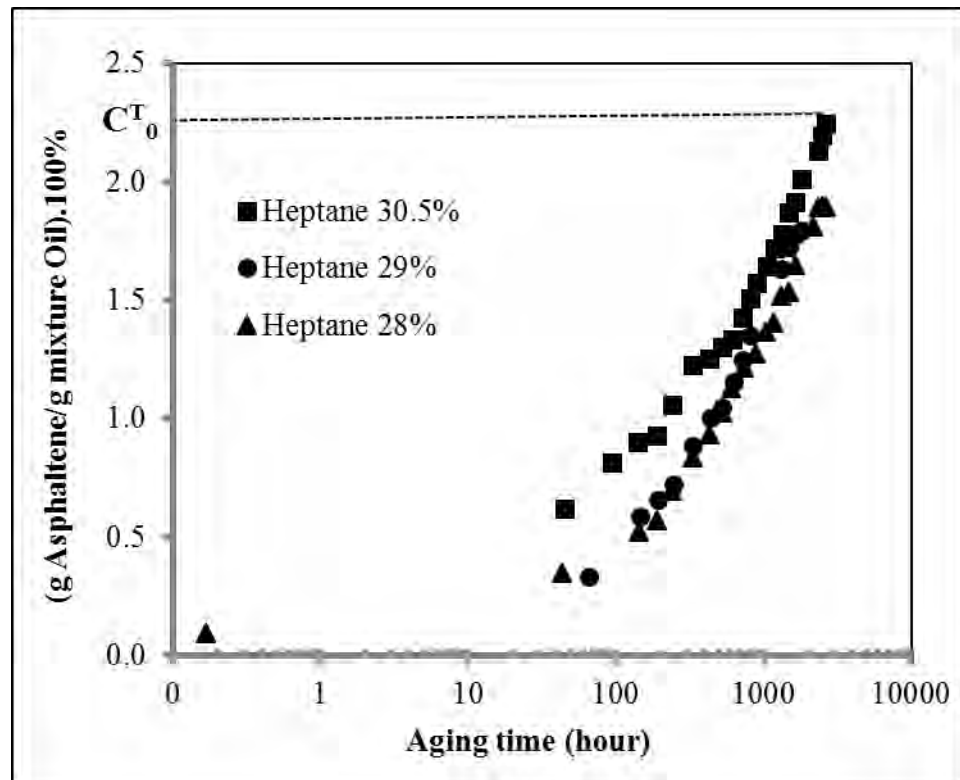
Initially, all asphaltenes in pure oil are stable asphaltenes. Right after heptane addition to crude oil at a given concentration, some asphaltenes become unstable and precipitate instantaneously. The unstable asphaltenes keep growing into the sizes that can be centrifuged. In this technique, few samples of the oil-heptane mixture are taken and centrifuged at 14000 rpm for 10 minutes over time as the mixture aged. After centrifugation, there will be a wet cake coming out to the bottom of the centrifuge tube that contains the centrifugable unstable asphaltenes. The concentration of unstable asphaltenes can further be calculated from dried cake, which is the wet cake after washing with heptane and drying in oven. Then, the concentration of unstable asphaltenes is plot against the aging time of oil-heptane mixture. For aging time is long enough, the coming out cake after centrifuging is supposed to contain all unstable asphaltenes. At this point, the concentration of

unstable asphaltenes is the plateau value from the plot of concentration of unstable asphaltenes as a function of aging time of oil-heptane mixture.

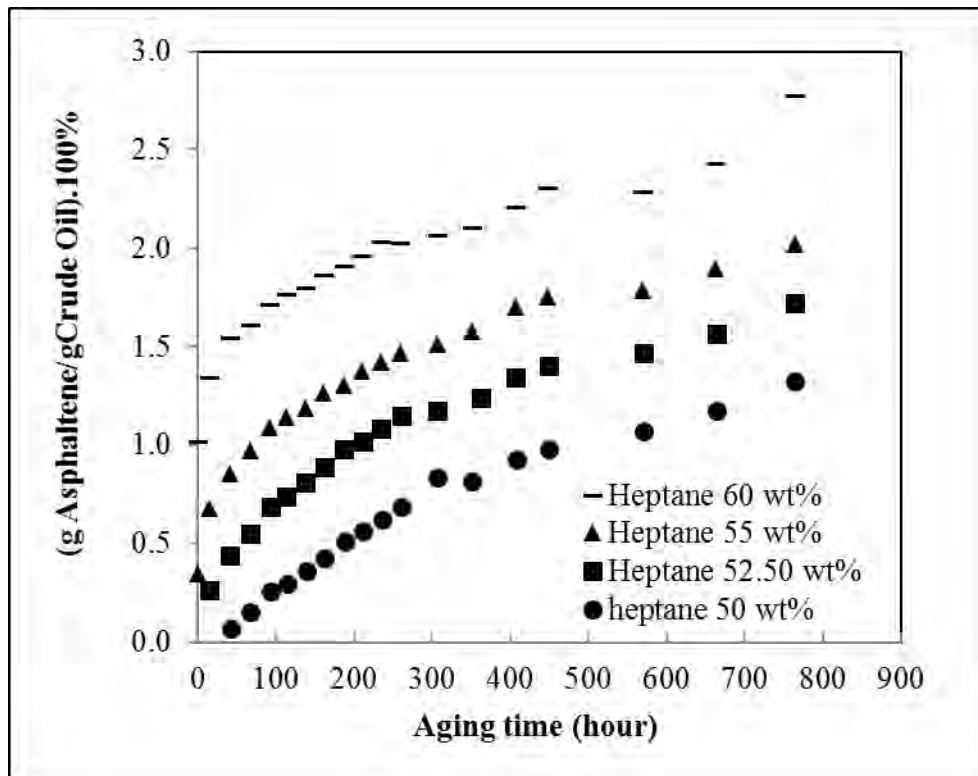
Following the same procedure, the centrifugation experiment was performed with aged Harry crude oil-heptane mixture with different heptane concentrations, which are 28, 29, and 30.5wt%. Figure 4.10 shows concentration of unstable asphaltenes as a function of aging time of the mixture at different heptane concentrations. As it is seen in the plots, also in Figure 4.11; which is in semi-log scale; there is no plateau value in concentration of unstable asphaltenes observed even over 2500 hours at heptane concentration around or below instantaneous. The same trend was also observed for Erin Crude oil, as shown in Figure 4.12 and 4.13.  $C_T^0$  is defined as a final concentration of unstable asphaltenes value in the plots for Harry crude oil and used for further calculation of deposition rate. This observed trend cannot be explained by the population balance from Maqbool *et al.*, 2011 assuming aggregation limited process. For low heptane concentration, it seems like kinetics is governed by a phenomenon other than aggregation kinetics.



**Figure 4.10** Concentration of unstable asphaltenes as a function of aging time of Harry crude oil-heptane mixture at different heptane concentrations.

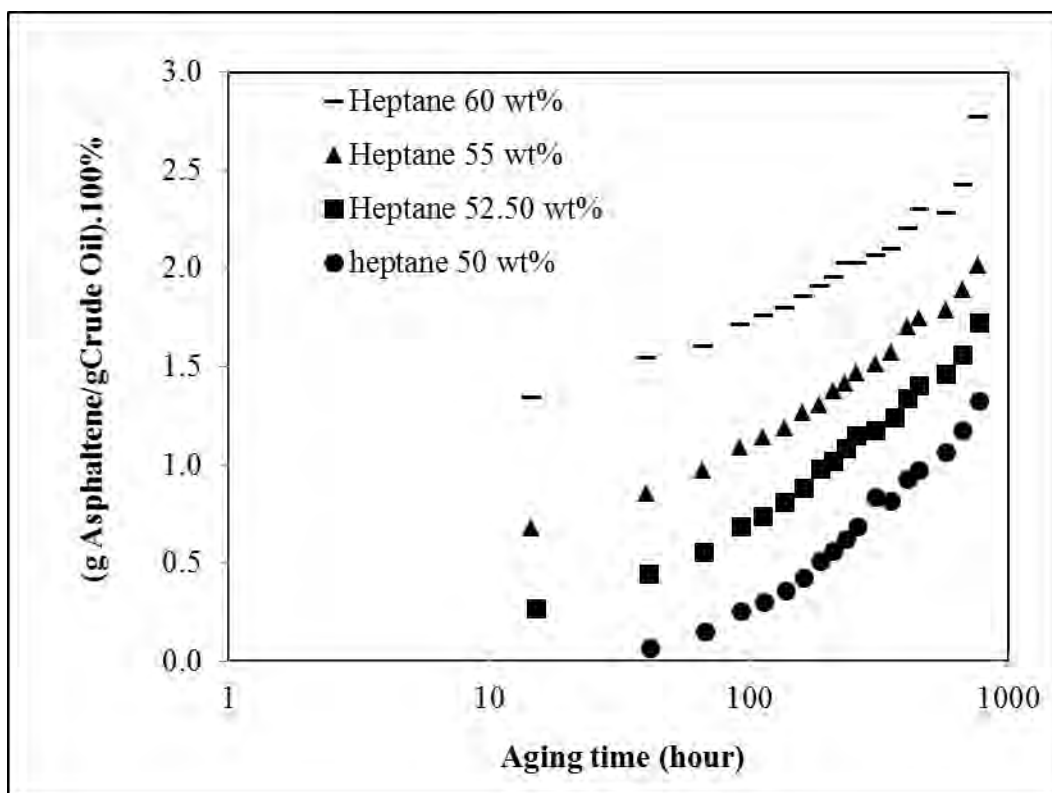


**Figure 4.11** Concentration of unstable asphaltene as a function of aging time in semi-log scale of Harry crude oil-heptane mixture at different heptane concentrations.



**Figure 4.12** Concentration of unstable asphaltenes as a function of aging time of Erin crude oil-heptane mixture at different heptane concentrations.



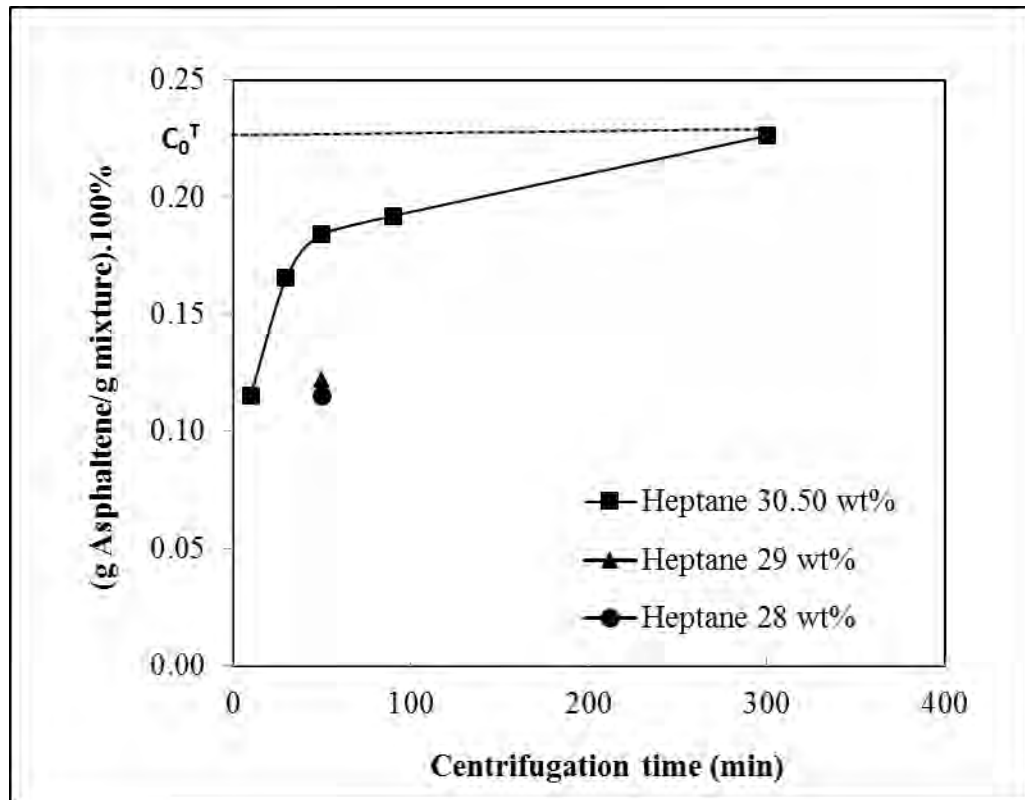


**Figure 4.13** Concentration of unstable asphaltenes as a function of aging time in semi-log scale of Erin crude oil-heptane mixture at different heptane concentrations.

Since the oil-heptane mixture that was fed into packed bed was fresh mixture, the technique to measure concentration of unstable asphaltenes based on centrifugation of aged oil-heptane mixture seems to have given an overestimated value of concentration of unstable asphaltenes.

To resolve the concentration of unstable asphaltenes for fresh oil-heptane mixture, centrifugation of fresh oil-heptane mixture at different centrifugation times was introduced to measure the concentration of unstable asphaltenes. In this technique, supernatant obtained after centrifuging could be used to perform deposition experiment to see if asphaltenes left in that supernatant affect deposition rate. Moreover, the same supernatant could also be used to perform detection time experiment to see if there is a consistency between unstable asphaltenes left in supernatant and in the cake at every centrifugation time. After heptane addition at a given concentration, the mixture was centrifuged for 10, 30, 50, and 300 minutes.

The result of concentration of unstable asphaltenes as a function of centrifugation time is shown in the Figure 4.14.

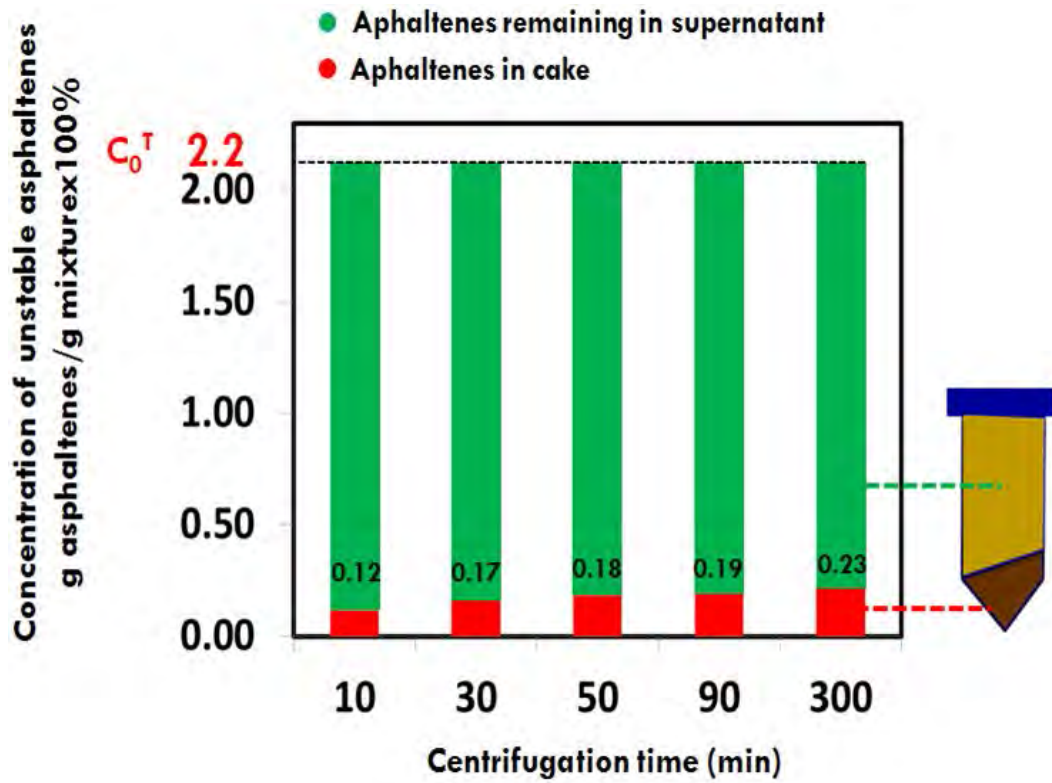


**Figure 4.14** Concentration of unstable asphaltenes as a function of centrifugation time of Harry crude oil-heptane mixture at different heptane concentrations.

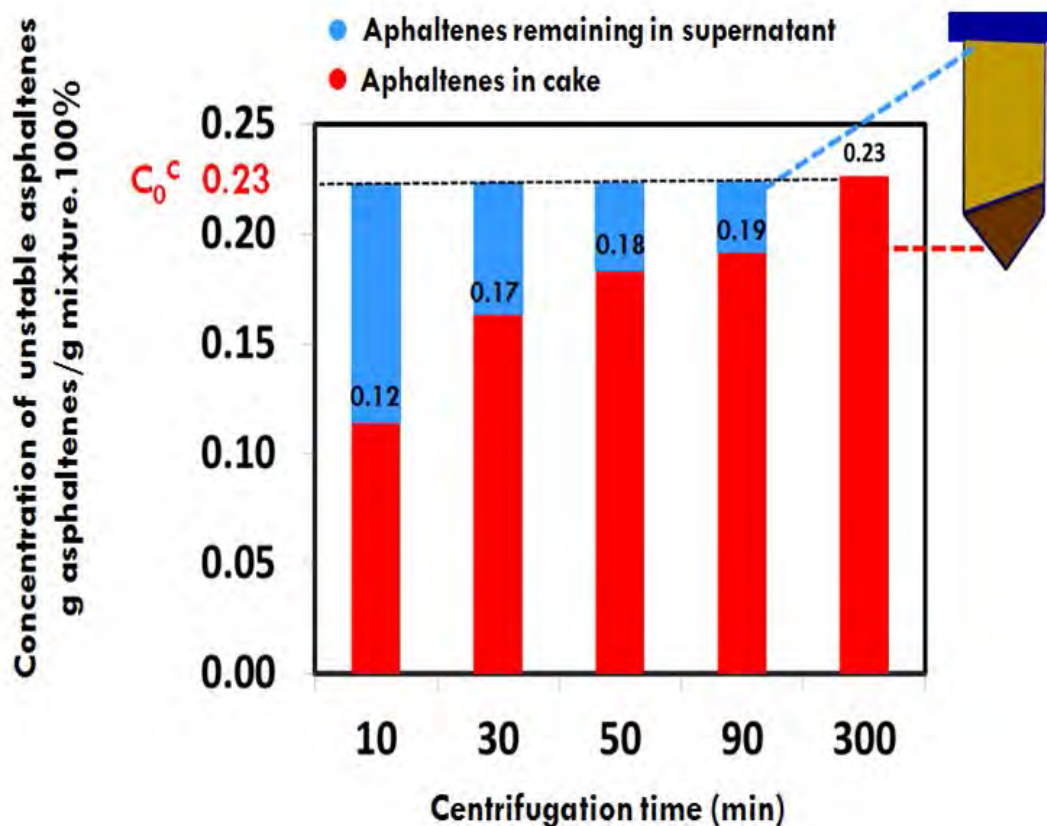
In this technique, 300 minutes was assumed to be enough to remove unstable asphaltenes in fresh oil-heptane mixture. As can be seen in Figure 4.14, the concentration of unstable asphaltene increases as centrifugation time increases. The final concentration is defined to be  $C_0^C$  for further calculation of deposition rate.

So far, there are two techniques to measure concentration of unstable asphaltens. The first one is the conventional technique based on centrifugation of aged oil-heptane mixture. The second technique is the technique that is proposed in this research. The following bar plots, Figure 4.15 and 4.16, show the difference in

concentration of unstable asphaltenes measured using these two techniques in quantified way.



**Figure 4.15** Bar plot showing concentration of unstable asphaltenes left in supernatant after centrifuging for different times, calculation based on centrifugation of aged Harry crude oil-heptane mixture, heptane 30.5 wt.%.

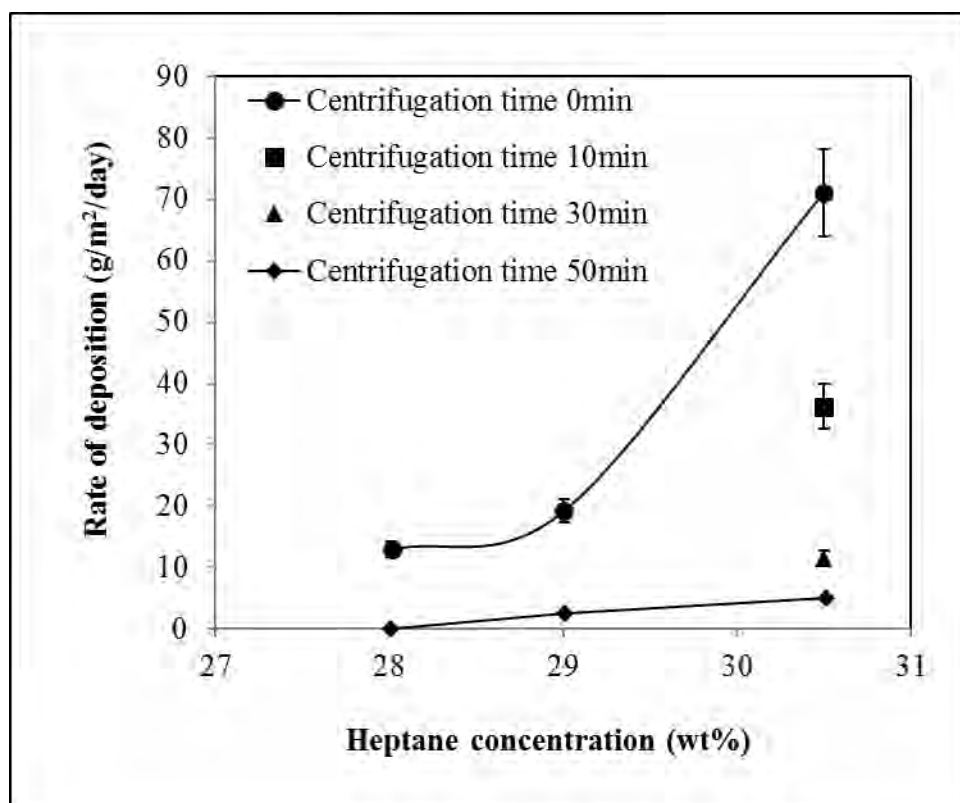


**Figure 4.16** Bar plot showing concentration of unstable asphaltene left in supernatant after centrifuging for different times, calculation based on 300 min-long centrifugation of fresh Harry crude oil-heptane mixture, heptane 30.5 wt.%.

As seen in Figure 4.15 and 4.16, concentration of unstable asphaltene in cake is the same at each centrifugation time, red parts of the plots, for both techniques. The difference is the concentration of unstable asphaltene remaining in supernatant. Centrifugation aged oil-heptane mixture technique gives 10 times higher in concentration of unstable asphaltene remaining in supernatant than long time centrifugation of fresh oil-heptane mixture technique.

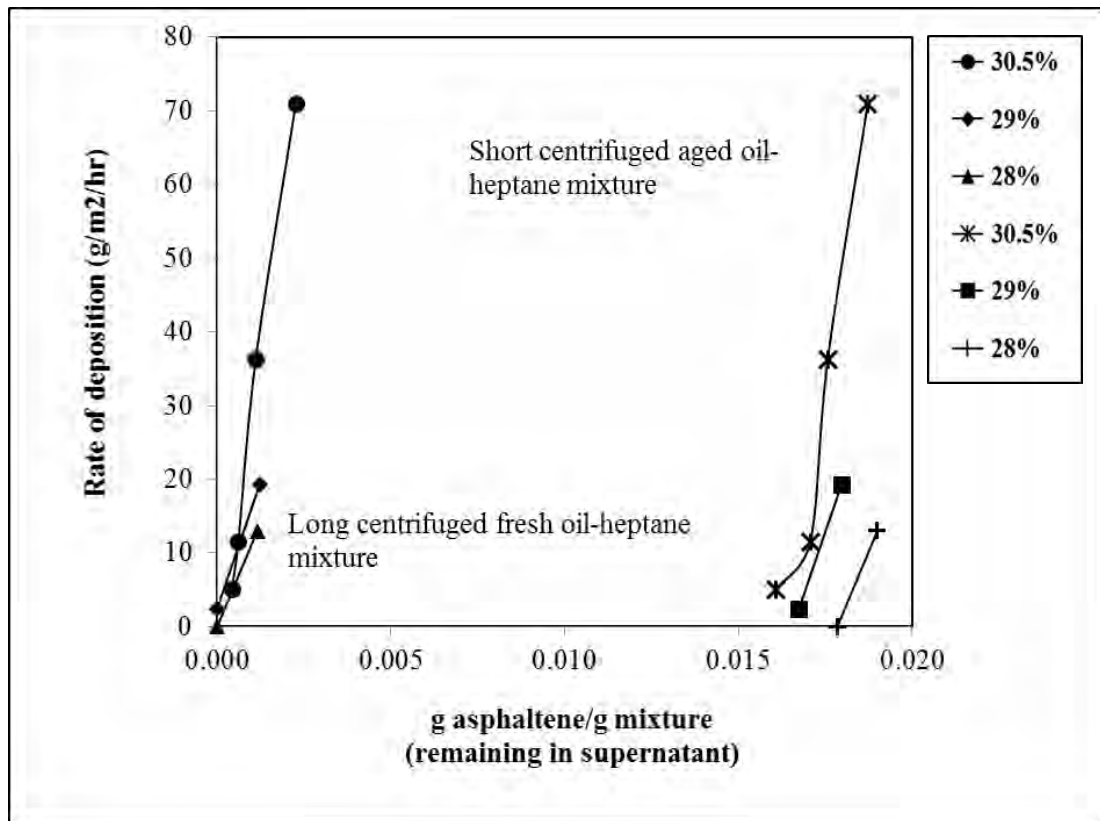
To find out how the concentration of unstable asphaltene remaining in supernatant after centrifuging fresh oil-heptane mixture affects deposition experiment, deposition experiments were performed with supernatant of fresh oil-heptane mixture at heptane concentrations 28, 29, and 30.5 wt%. The results are shown in Figure 4.17. The results show that increasing in heptane concentration

results in an increase in rate of deposit at a given centrifugation time. Moreover, at a given heptane concentration, rate of deposition drops down with centrifugation time goes down.



**Figure 4.17** Rate of deposition at different centrifugation times as a function of heptane concentration.

Since there two concentrations of unstable asphaltnes obtained from two different techniques and one deposition rate at a given heptane concentration and centrifugation time, the rate of depositions as a function of the concentrations of unstable asphaltenes were plot together as shown in Figure 4.18.

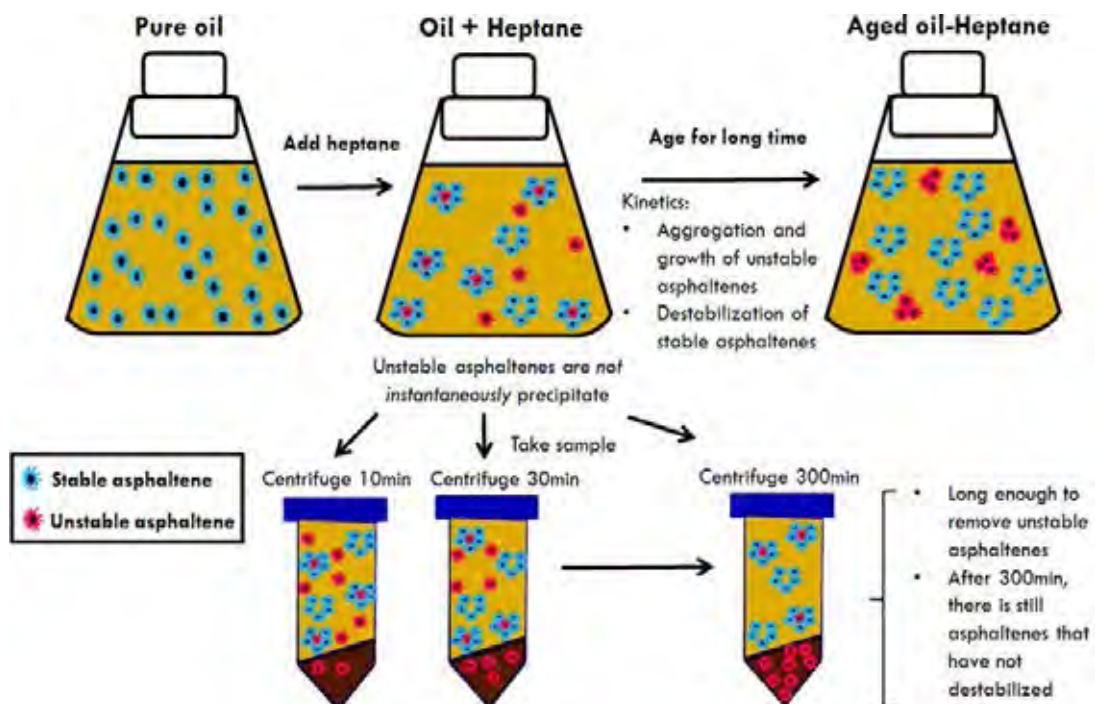


**Figure 4.18** Rate of deposition as a function of concentration of unstable asphaltenes obtained from long centrifuged (300 min) fresh oil-heptane mixture and short centrifuged (10min) aged oil-heptane mixture.

Results in Figure 4.18 shows that concentration of unstable asphaltenes of aged oil-heptane mixture overestimates concentration of unstable asphaltenes of fresh oil-heptane mixture. The results also suggest that there is kinetics of asphaltenes destabilization.

Asphaltene deposition rate as a function of concentration of unstable asphaltenes based on fresh mixture crosses the axis origin (0, 0), meaning that asphaltene deposition in packed bed responds to the concentration of unstable asphaltenes obtained from fresh oil-heptane mixture. Extensively, diffusivity is calculated based on concentration of unstable asphaltenes of fresh oil-heptane mixture, giving an approximated value  $2 \times 10^{-11} \text{m}^2/\text{s}$ .

The long centrifugation of fresh oil-heptane mixture technique gives a good respond to deposition in packed bed than the short centrifugation of aged oil-heptane mixture technique. There is a possible explanation as shown in Figure 4.19.

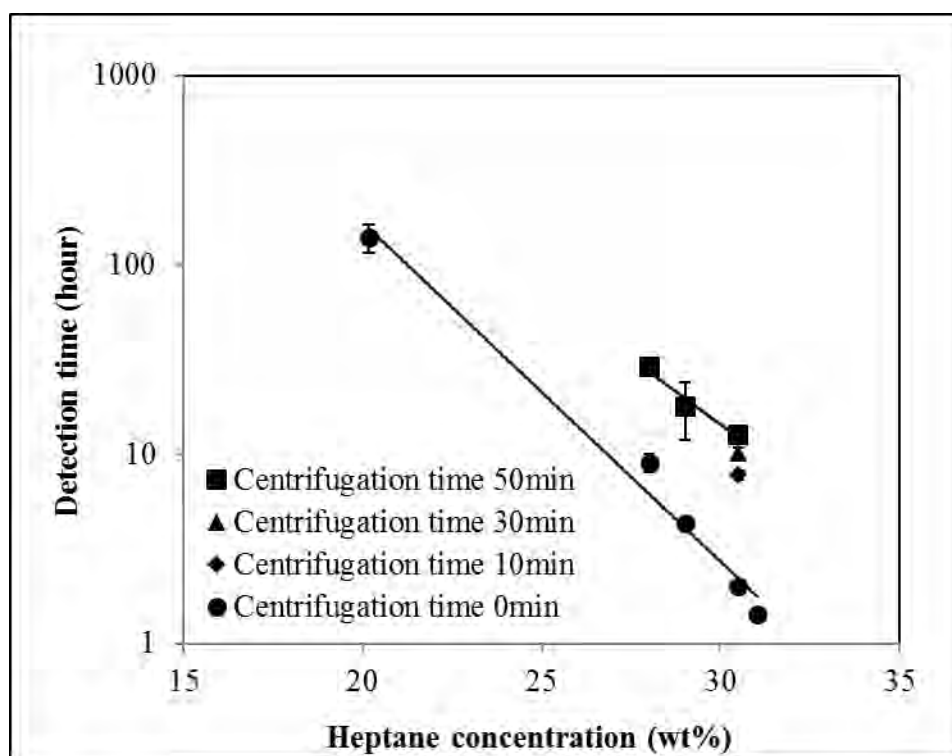


**Figure 4.19** Schematic illustrating the method measuring concentration of unstable asphaltenes of fresh oil-heptane mixture.

First, all asphaltenes in pure oil are stable asphaltenes. Right after adding heptane into oil, some asphaltenes become unstable. They do not instantaneously precipitate, meaning that some of the unstable asphaltenes precipitate, but some of them may be trapped by stable asphaltenes. If the oil-heptane mixture is aged for long time, all unstable asphaltenes will be released or destabilized from stable asphaltenes and undergo aggregation and growth to be larger sizes. In our study, the oil-heptane mixture would not be aged. Right after heptane addition, few samples were withdrawn and centrifuged for different times such as, 10, 30, 50, and 300 minutes. Assume that 300 minutes is a centrifugation time long enough to remove all unstable asphaltenes have been released from stable asphaltenes and after this time there is still asphaltenes that have not been released.

The concentration of unstable asphaltenes obtained from 300 min-long centrifugation of the mixture is supposed to be the concentration contributing to real deposition process rather than the other, which there may be some uncertainties of asphaltenes due to aging time.

Along with the deposition experiments, detection time experiments were performed with the supernatant at each centrifugation time. The results in Figure 4.20 show that at a given centrifugation time, increasing in heptane concentration results in a decrease in detection time. In addition, at a given heptane concentration, there is an increase in detection time as centrifugation time increases. The detection time measurement of centrifuged oil-heptane mixtures is likely probing the kinetics of asphaltene destabilization not exclusively kinetics of aggregation.



**Figure 4.20** Detection time as a function of Heptane concentration at each centrifugation time.



## **CHAPTER V**

### **CONCLUSIONS AND RECOMMENDATIONS**

#### **5.1 Conclusions**

In this study, effects of bead size and concentration of unstable asphaltenes obtained from different centrifugation techniques on asphaltene deposition has been investigated using packed bed apparatus. In the former effect, different size of bead or stainless steel spheres such as 2 mm, and 3 and 4 mm (packed together) were used in order to perform asphaltene the deposition experiments. Extensively, the diffusion-limited deposition model or mass-transfer limited deposition model was also used to predict the mass of deposited material respected to experimental data. It has been revealed that the diffusion-limited deposition model successfully explains asphaltene deposition in packed bed of 2 mm beads, which is the bead size that the model has not previously been used to predict mass of deposit. So the 2 mm bead size can be probably used for higher flow rate asphaltene deposition experiment. Moreover, the model give a good agreement with the experimal data, meaning that the model captures the effect of bead size on asphaltene deposition in packed bed apparatus.

In the later effect, a new technique to measure concentration of unstable stable asphaltenes, which is long centrifugation of fresh oil-heptane mixture was introduced to compare with the centrifugation of aged oil-heptane mixture. It has been found out that the concentration of unstable asphaltenes obtained from fresh oil-heptane mixture differs from the concentration of unstable asphaltenes obtained from aged oil-heptane mixture. The results indicate that there is an existence of destabilization kinetics.

#### **5.2 Recommendations**

In this study, the effect of bead size on asphaltene deposition, 3 and 4 mm have been performed at flow rates higher than 0.9 g/min; which is the flow rate that is focus in this investigation, and already proved by the diffusion-limited deposition

model, but 2 mm bead size has been used at only one flow rate, which is 0.9 g/min. The recommendation on this effect would be running asphaltene deposition experiment using packed bed packed with 2 mm bead size at higher flow rates and different crude oils to validate the model.

Speaking of running asphaltene deposition experiment at high flow rate, it could be performed by recycling oil-heptane mixture reservoir in a loop to reduce amount of crude oil used. To perform this kind of experiment, a certain reservoir size is needed to prevent depletion of asphaltenes in the reservoir. To use this method, a total unstable asphaltene concentration in the reservoir need to be measured. Instead of using the centrifugation of aged oil-heptane mixture to measure the total concentration of unstable asphaltenes, the centrifugation of fresh oil-heptane mixture would highly be recommended.

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## APPENDICES

### Appendix A Data of Detection Time Experiment of Harry Crude Oil

**Table A1** Data of detection time experiment of Harry crude oil before performing asphaltene deposition experiment

Heptane concentration (wt.%)	Detection time (Hour)	Averaged detection time (Hour)	STD of detection time (Hour)
31.01	1.33	1.42	0.08
31.01	1.50		
30.50	2	2	0
30.01	3	3.17	0.17
30.01	3.33		
29.02	4.33	4.33	0
28.20	8	9	1
28.04	10		
20.18	122	139.67	23.24
20.18	124.5		
20.18	172.5		

### Appendix B Nomenclature

$A_c$  = Cross-sectional area of empty column ( $m^2_{col}$ )

$C_{A0}$  = Concentration of unstable asphaltenes in reservoir ( $\frac{kg}{m^3}$ )

$D$  = Diffusivity of asphaltenes ( $\frac{m^2}{s}$ )

$d_B$  = Diameter of bead (m)

$J$  = Rate of asphaltene deposition ( $\frac{kg}{s}$ )

$m$  = Mass of asphaltenes deposited in packed bed (g)

- L = length of packed bed (m)
- q = Mass flow rate  $\left(\frac{\text{kg}}{\text{s}}\right)$
- t = Run-time (s)
- $\emptyset$  = Void fraction (porosity) of packed bed
- $\rho$  = Density of fluid  $\left(\frac{\text{kg}}{\text{m}^3}\right)$
- $\mu$  = Viscosity of fluid  $\left(\frac{\text{kg}}{\text{ms}}\right)$

## Appendix C Information of Packed Bed

**Table C1** Information of packed bed packed with 2 mm spheres

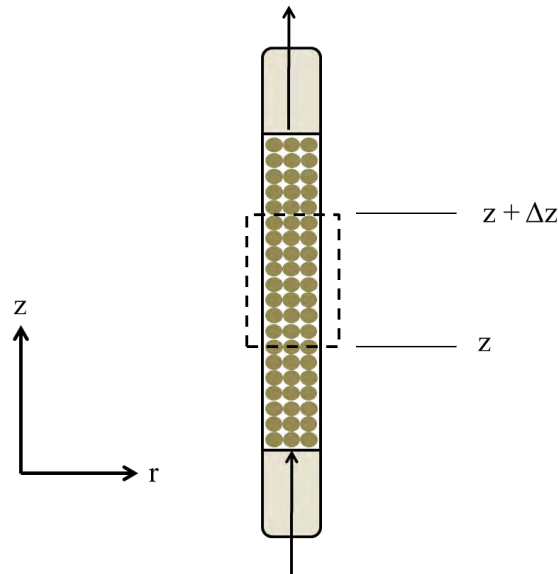
	#	mm	m	m <sup>2</sup>	m <sup>3</sup>	L	mL
Diameter Column	-	10	0.01	-	-	-	-
Cross Sectional Area Column	-	-	-	7.85E-05	-	-	-
Height Column	-	300	0.3	-	-	-	-
Volume Empty Column	-	-	-	-	2.36E-05	2.36E-02	23.56
Diameter 2-mm bead	-	2	0.002	-	-	-	-
Volume 2-mm bead	-	-	-	-	4.19E-09	4.19E-06	0.00419
Height Packed Bed	-	132	0.132	-	-	-	-
# 2-mm spheres in packed bed	~1511	-	-	-	-	-	-
Volume void in packed bed	-	-	-	-	4.04E-06	4.04E-03	4.038E+00
Porosity packed bed (void fraction)	0.3895	-	-	-	-	-	-

**Table C2** Information of packed bed packed with 3 mm and 4mm spheres

	#	mm	m	m <sup>2</sup>	m <sup>3</sup>	L	mL
Diameter Column	-	10	0.01	-	-	-	-
Cross Sectional Area Column	-	-	-	7.85E-05	-	-	-
Height Column	-	300	0.3	-	-	-	-
Volume Empty Column	-	-	-	-	2.36E-05	2.36E-02	23.56
Diameter 3-mm bead	-	3	0.003	-	-	-	-
Volume 3-mm bead	-	-	-	-	1.41E-08	1.41E-05	0.014
Diameter 4-mm bead	-	4	0.004	-	-	-	-
Volume 4-mm bead	-	-	-	-	3.35E-08	3.35E-05	0.034
Height Packed Bed	-	132	0.132	-	-	-	-
# 3-mm spheres in packed bed	36	-	-	-	-	-	-
# 4-mm spheres in packed bed	148	-	-	-	-	-	-
Volume void in packed bed	-	-	-	-	4.90E-06	4.90E-03	4.899E+00
Average Sphere Diameter	-	3.804	0.003804	-	-	-	-
Average Sphere Projected Area	-	-	-	1.13E-05	-	-	-
Porosity packed bed (void fraction)	4.73E-01	-	-	-	-	-	-



### Appendix D A Mass-Transfer Limited Deposition Model (Hanpan, 2016)



**Figure D1** Packed bed column. Control volume is show in dash line box.

A mass balance of asphaltenes was performed in control volume of the packed bed column as show in Figure D1. The equation could be expressed as:

$$F_A|_z - F_A|_{z+\Delta z} - J_A a_c A_c \Delta z = 0 \quad (\text{D.1})$$

$$\frac{-(F_A|_z - F_A|_{z+\Delta z})}{\Delta z} - J_A a_c A_c = 0$$

- Where
- $F_A$  = Mass flow rate of asphaltenes  $\left(\frac{\text{kg}}{\text{s}}\right)$
  - $J_A$  = Flux of asphaltenes towards bead surface  $\left(\frac{\text{kg}}{\text{m}^2 \text{ surface s}}\right)$
  - $a_c$  = Total surface area per volume of empty column  $\left(\frac{\text{m}^2 \text{ surface}}{\text{m}^3 \text{ col}}\right)$
  - $A_c$  = Cross-sectional area of empty column  $(\text{m}^2_{\text{col}})$
  - $\Delta z$  = Height of differential control volume  $(\text{m}_{\text{col}})$

Take the limit as  $\Delta z \rightarrow 0$

$$-\frac{dF_A}{dz} - J_A a_c A_c = 0 \quad (D.2)$$

The asphaltenes move in the axial direction by convection, so

$$F_A = UA_c C_A \quad (D.3)$$

Where  $U$  = Superficial velocity  $\left(\frac{m}{s}\right)$

It is hypothesized that the flux of asphaltenes towards bead surface is due to the concentration gradient between the asphaltenes in the bulk solution and on the bead surface. Note that, the operated flow rates are very low ( $Re \ll 1$ ), so the fluid will move parallel to the bead surface. The asphaltene deposition rate,  $J_A$ , can be expressed as:

$$J_A = \frac{D}{\delta} (C_A - C_{A,s}) \quad (D.4)$$

Where  $D$  = Diffusivity of asphaltenes  $\left(\frac{m^2}{s}\right)$

$\delta$  = Mass-transfer boundary layer thickness (m)

$C_A$  = Concentration of unstable asphaltenes in solution  $\left(\frac{kg}{m^3}\right)$

$C_{A,s}$  = Concentration of unstable asphaltenes on bead surface  $\left(\frac{kg}{m^3}\right)$

By assuming that the rate of surface reaction is faster than the rate of mass transfer towards the surface, a mass balance can be performed on the bead surface to relate concentration of asphaltenes on bead surface with the measurable parameters.

$$\frac{D}{\delta} (C_A - C_{A,s}) = k_r C_{A,s} \quad (D.5)$$

$$C_{A,s} = C_A \left( \frac{\frac{D}{\delta}}{\frac{D}{\delta} + k_r} \right) \quad (D.6)$$

The ratio of the diffusivity,  $D$ , to the boundary layer thickness,  $\delta$ , is the mass transfer coefficient, i.e.,

$$k_c = \frac{D}{\delta} \quad (\text{D.7})$$

Substitution of equation D.6 and D.7 into equation D.4, therefore the asphaltene deposition rate is

$$J_A = k_c \left( C_A - \frac{C_A k_c}{k_c + k_r} \right)$$

$$J_A = \frac{k_c k_r}{k_c + k_r} C_A \quad (\text{D.8})$$

Where  $k_c$  = Mass-transfer coefficient  $\left(\frac{\text{m}}{\text{s}}\right)$   
 $k_r$  = Reaction rate constant  $\left(\frac{\text{m}}{\text{s}}\right)$

Substitution of equation D.3 and D.8 into equation D.2, hence

$$-\frac{UA_c dC_A}{dz} - \frac{k_c k_r}{k_c + k_r} C_A a_c A_c = 0$$

$$\frac{dC_A}{dz} + \frac{k_c k_r}{U k_c + k_r} C_A a_c = 0 \quad (\text{D.9})$$

Let  $\theta = \frac{C_A}{C_{A0}}$ , where  $C_{A0}$  is inlet concentration of unstable asphaltenes  $\left(\frac{\text{mol}}{\text{m}^3}\right)$ .

Substitution of this expression into equation D.9 gives

$$\frac{d\theta}{dz} + \frac{k_c k_r}{U k_c + k_r} \theta a_c = 0 \quad (\text{D.10})$$

Let  $\xi = \frac{z}{L}$ , where  $L$  = length of the packed bed (m), Substitution of this expression into equation D.10 gives the resulting problem statement, in dimensionless form, as

$$\frac{d\theta}{Ld\xi} + \frac{k_c}{U} \frac{k_r}{k_c+k_r} \theta La_c = 0 \quad (D.11)$$

Putting  $a_c = \frac{6(1-\emptyset)}{d_B}$  into equation D.11

$$\frac{d\theta}{d\xi} + \frac{k_c}{U} \frac{k_r}{k_c+k_r} \theta \frac{6L(1-\emptyset)}{d_B} = 0 \quad (D.12)$$

For flow through a packed bed, the correlation of Sh given by D. Thoenes and H. Kramers (1957) is expressed as:

$$Sh = 1.0Re^{\frac{1}{2}}Sc^{\frac{1}{3}} \quad (D.13)$$

Where

$$Sh = \frac{\emptyset k_c d_B}{(1-\emptyset)\gamma D}$$

$$Re = \frac{\rho U d_B}{(1-\emptyset)\gamma \mu}$$

$$Sc = \frac{\mu}{\rho D}$$

$\emptyset$  = Void fraction (porosity) of packed bed  
 $d_B$  = Diameter of bead (m)  
 $\gamma$  = Shape factor, equals surface area divided by  $\pi d^2$   
 $\rho$  = Density of fluid  $\left(\frac{kg}{m^3}\right)$   
 $\mu$  = Viscosity of fluid  $\left(\frac{kg}{ms}\right)$

Consider the ratio of Sh to Re and Sc

$$\frac{Sh}{ReSc} = \left(\frac{\emptyset k_c d_B}{(1-\emptyset)\gamma D}\right) \left(\frac{(1-\emptyset)\gamma \mu}{\rho U d_B}\right) \left(\frac{\rho D}{\mu}\right)$$

$$\frac{Sh}{ReSc} = \frac{\emptyset k_c}{U} \quad (D.14)$$

Substitution of equation D.14 into equation D.12, thus

$$\frac{d\theta}{d\xi} + \frac{Sh}{ReSc\phi} \frac{k_r}{k_c+k_r} \theta^{\frac{6L(1-\phi)}{d_B}} = 0 \quad (D.15)$$

By making  $\lambda = \frac{6L(1-\phi)}{\phi}$ , the equation D.15 can be rearranged as:

$$\frac{d\theta}{d\xi} + \frac{Sh}{ReSc} \frac{\lambda k_r}{k_c+k_r} \theta = 0 \quad (D.16)$$

Assuming that the system is mass-transfer limited, so  $\frac{k_r}{k_c+k_r} = 1$ . The equation D.16 would be written as:

$$\frac{d\theta}{d\xi} + \frac{Sh}{ReSc} \lambda \theta = 0 \quad (D.17)$$

This differential equation, when solved, describes the concentration of unstable asphaltenes as a function of  $z$ . The boundary condition is

$$\text{B.C.1:} \quad \text{at } \xi = 0, \theta = 1 \quad (D.18)$$

Substitution of this boundary condition into equation D.17 finally gives

$$\theta = e^{\frac{-Sh}{ReSc} \lambda \xi} \quad (D.19)$$

Hence mass of asphaltenes deposited in packed bed (g),  $m_{dep}$ , can be expressed as:

$$m_{dep} = (F_A|_{\xi=0} - F_A|_{\xi=1})t \quad (D.20)$$

$$m_{dep} = C_{A0} U A_C t (1 - \theta|_{\xi=1})$$

$$m_{\text{dep}} = C_{A0} U A_c t \left( 1 - e^{-\frac{Sh}{ReSc} \lambda} \right) \quad (\text{D.21})$$

Where  $C_{A0}$  = Concentration of unstable asphaltenes in reservoir  $\left( \frac{\text{kg}}{\text{m}^3} \right)$

$U$  = Superficial velocity  $\left( \frac{\text{m}}{\text{s}} \right)$

$A_c$  = Cross-sectional area of empty column  $(\text{m}^2_{\text{col}})$

$t$  = Run-time (s)

$$Sh = \frac{\phi k_c d_B}{(1-\phi) \gamma D}$$

$$Re = \frac{\rho U d_B}{(1-\phi) \gamma \mu}$$

$$Sc = \frac{\mu}{\rho D}$$

$$\lambda = \frac{6L(1-\phi)}{\phi}$$

The asphaltene deposition rate  $\left( \frac{\text{kg}}{\text{s}} \right)$  in packed bed, J, is expressed as

$$J = C_{A0} U A_c (1 - \theta) \quad (\text{C.22})$$

Where  $\theta = e^{-\frac{Sh}{ReSc} \lambda}$

When the length of packed bed is very short,

$$1 - e^{-\frac{Sh}{ReSc} \lambda} \approx \frac{Sh}{ReSc} \lambda$$

$$1 - \theta \approx \frac{Sh}{ReSc} \lambda \quad (\text{D.23})$$

Substitution of equation D.23 into equation D.22 gives

$$J = C_{A0} U A_c \frac{Sh \lambda}{ReSc} \quad (\text{D.24})$$

Substitution of Sh correlation (equation D.13) into equation D.24 gives

$$J = C_{A0} U A_C \lambda \text{Re}^{\frac{-1}{2}} \text{Sc}^{\frac{-2}{3}} \quad (\text{D.25})$$

Substitution of Re and Sc correlations into equation D.25 gives

$$J = C_{A0} U A_C \lambda \left( \frac{\rho U d_B}{(1-\emptyset) \gamma \mu} \right)^{\frac{-1}{2}} \left( \frac{\mu}{\rho D} \right)^{\frac{-2}{3}} \quad (\text{D.26})$$

Finally, the equation D.26 is simplified as

$$J = \frac{6L(1-\emptyset)^{\frac{5}{2}}}{\emptyset} A_C^{\frac{1}{2}} d_B^{\frac{-3}{2}} \mu^{\frac{-1}{6}} \rho^{\frac{-1}{3}} D^{\frac{2}{3}} C_{A0} q^{\frac{1}{2}} \quad (\text{D.27})$$

- Where
- J = Rate of asphaltene deposition  $\left( \frac{\text{kg}}{\text{s}} \right)$
  - L = length of packed bed (m)
  - $\emptyset$  = Void fraction (porosity) of packed bed
  - $A_c$  = Cross-sectional area of empty column  $(\text{m}^2_{\text{col}})$
  - $d_B$  = Diameter of bead (m)
  - $\mu$  = Viscosity of fluid  $\left( \frac{\text{kg}}{\text{ms}} \right)$
  - $\rho$  = Density of fluid  $\left( \frac{\text{kg}}{\text{m}^3} \right)$
  - D = Diffusivity of asphaltenes  $\left( \frac{\text{m}^2}{\text{s}} \right)$
  - $C_{A0}$  = Concentration of unstable asphaltenes in reservoir  $\left( \frac{\text{kg}}{\text{m}^3} \right)$
  - q = Mass flow rate  $\left( \frac{\text{kg}}{\text{s}} \right)$

## Appendix E Data of Asphaltene Deposition Experiments of Effect of Bead Size

**Table E1** Experimental data of asphaltene deposition experiment of effect of bead size

dB (m)	$\phi$ (porosity)	$\alpha$ (m <sup>-3/2</sup> )	m (mass of deposit) (g)	Specific rate (g/m <sup>2</sup> /day)	Rate of deposition (g/hr)
0.002	0.39	13693	0.4189	66.3175	0.0589
0.0038	0.47	3461	0.1996	70.9649	0.0250



**Table E2** Fitting Data of Asphaltene Deposition Experiment of Effect of Bead Size Using Limited-Diffusion Deposition Model

Experimental data fitting			Upper boundary fitting			Lower boundary fitting		
D = 1.30E-11 m <sup>2</sup> /s			D = 2.20E-11 m <sup>2</sup> /s			D = 1E-11 m <sup>2</sup> /s		
$\alpha$	$\beta$	Rate (g/hr)	$\alpha$	$\beta$	Rate (g/hr)	$\alpha$	$\beta$	Rate (g/hr)
3000	0.0257	1.53E-02	3000	0.0257	2.18E-02	3000	0.0257	1.29E-02
4000	0.0257	2.05E-02	4000	0.0257	2.90E-02	4000	0.0257	1.72E-02
5000	0.0257	2.56E-02	5000	0.0257	3.63E-02	5000	0.0257	2.15E-02
6000	0.0257	3.07E-02	6000	0.0257	4.36E-02	6000	0.0257	2.58E-02
7000	0.0257	3.58E-02	7000	0.0257	5.08E-02	7000	0.0257	3.01E-02
8000	0.0257	4.09E-02	8000	0.0257	5.81E-02	8000	0.0257	3.43E-02
9000	0.0257	4.60E-02	9000	0.0257	6.54E-02	9000	0.0257	3.86E-02
10000	0.0257	5.11E-02	10000	0.0257	7.26E-02	10000	0.0257	4.29E-02
11000	0.0257	5.62E-02	11000	0.0257	7.99E-02	11000	0.0257	4.72E-02
12000	0.0257	6.14E-02				12000	0.0257	5.15E-02
13000	0.0257	6.65E-02				13000	0.0257	5.58E-02
14000	0.0257	7.16E-02				14000	0.0257	6.01E-02

\*Note:  $\alpha = dB^{(-3/2)}*((1-\phi)^{(3/2)})/\phi$ ,  $\beta = 6*Ac^{(1/2)}*L*C_{A0}*\rho^{(-1/2)}*\mu^{(-1/6)}*q^{(1/2)}*1000$

## Appendix F Data of Centrifugation Experiments

**Table F1** Data of centrifugation experiment of aged oil-hepatne mixture at various heptane concentration

Heptane Concentration = 30.5 wt.%		Heptane Concentration = 29 wt.%		Heptane Concentration = 28 wt.%	
Aging time (hr)	Averaged (g Asphaltene ppt/g mixture).100%	Aging time (hr)	Averaged (g Asphaltene ppt/g mixture).100%	Aging time (hr)	Averaged (g Asphaltene ppt/g mixture).100%
0.00	0.09	0.00	0.09	0.17	0.10
44.48	0.62	65.95	0.34	42.78	0.35
93.92	0.81	146.83	0.59	142.25	0.52
140.85	0.90	191.68	0.66	190.88	0.57
191.03	0.93	245.32	0.72	239.88	0.70
238.42	1.06	334.10	0.88	333.77	0.84
333.22	1.23	433.57	1.00	430.95	0.93
430.40	1.26	527.93	1.05	527.22	1.03
524.40	1.30	632.58	1.16	608.13	1.13
621.18	1.34	718.72	1.25	740.38	1.22
718.37	1.43	815.33	1.35	886.08	1.27
813.13	1.51	1320.33	1.64	1028.35	1.37

907.35	1.57	1490.60	1.73	1170.77	1.41
1053.05	1.64	1657.38	1.78	1314.37	1.52
1195.32	1.72	1823.88	1.80	1482.77	1.54
1337.73	1.78			1652.00	1.65
1649.73	1.87			2157.00	1.81
1818.97	1.92			2327.27	1.89
2323.97	2.01			2494.05	1.90
2494.23	2.13			2660.55	1.89
2661.02	2.20				
1337.73	2.25				
1649.73	0.09				
1818.97	0.62				
2323.97	0.81				
2494.23	0.90				
2661.02	0.93				

**Table F2** Data of centrifugation experiment of fresh oil-hepatne mixture at various heptane concentration

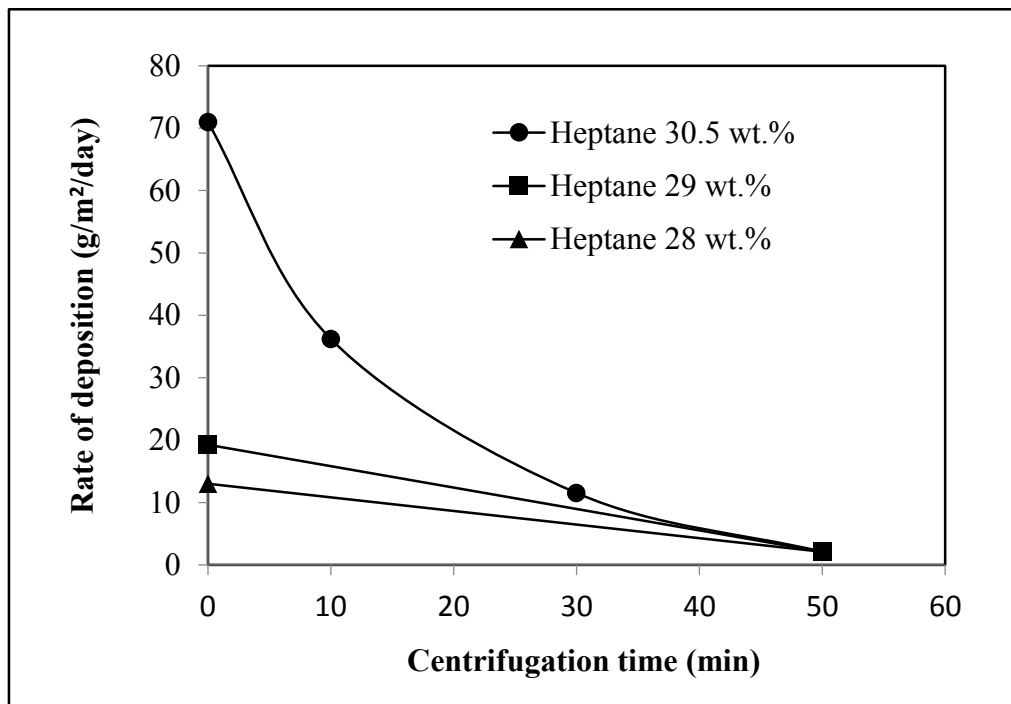
Centrifugation time (min)	Averaged (g Asphaltene ppt/g mixture).100%		
	Heptane Concentration = 30.5 wt.%	Heptane Concentration = 29 wt.%	Heptane Concentration = 28 wt.%
10	0.1154		
30	0.1653		
50	0.1840	0.1155	0.1221
90	0.1920		
300	0.2262		

**Appendix G Detection Time of Supernatant at Various Centrifugation Time and Heptane Concentration**

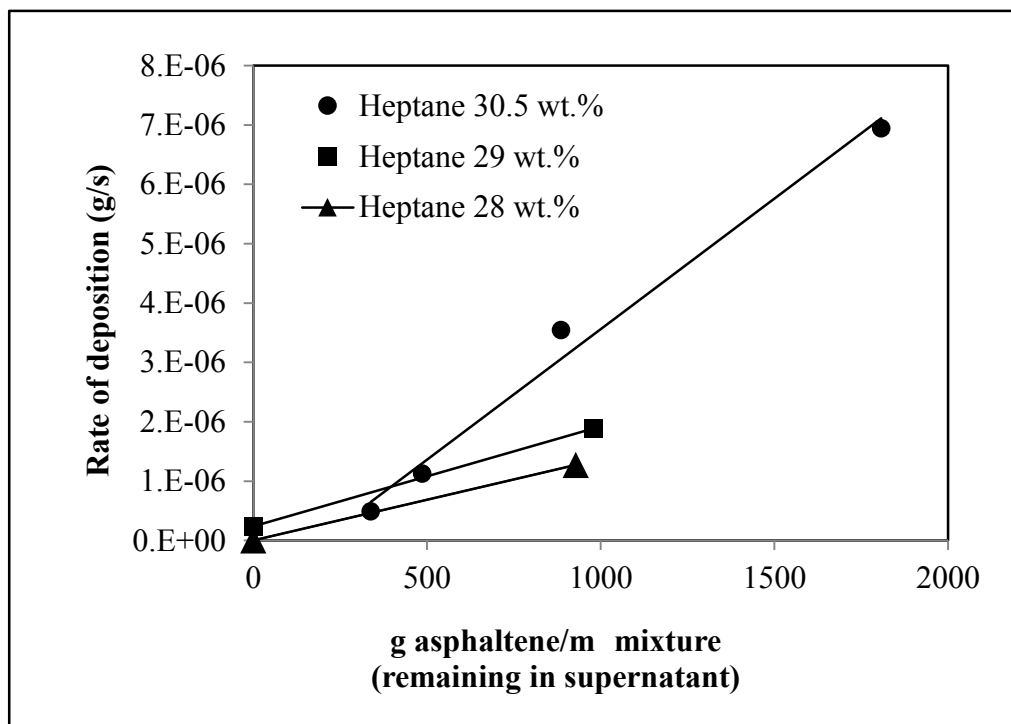
**Table G1** Detection time of supernatant at various centrifugation time and heptane concentration

Heptane Concentration (wt.%)	Centrifugation time (min)	Averaged Detection time (hr)	STD of Detection time (hr)
28	0	9	1
28	50	28.89	0.89
29	0	4.33	0
29	50	17.92	6.08
30.5	0	2	0
30.5	10	7.75	0.42
30.5	30	10.13	0.63
30.5	50	12.70	0.49
28	0	9	1

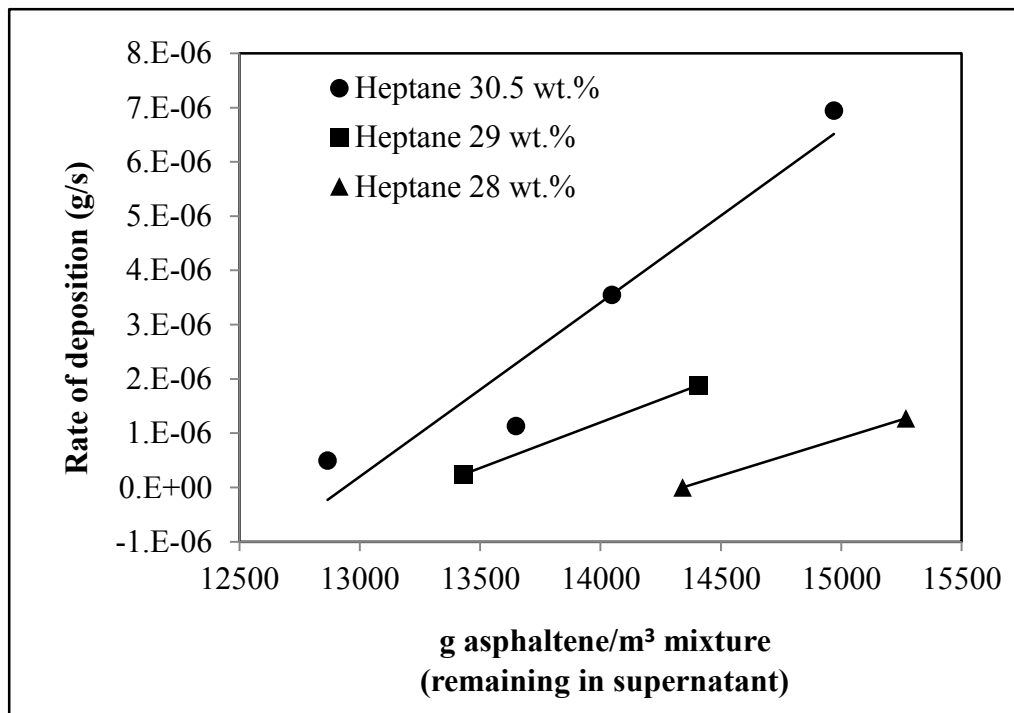
## Appendix H Effect of Concentration of Unstable Asphaltenes on Asphaltene Deposition Experiment



**Figure H1** Rate of asphaltene deposition as a function of centrifugation time at various heptane concentrations.



**Figure H2** Rate of asphaltene deposition as a function of concentration of unstable asphaltenes obtained from centrifugation of fresh oil-heptane mixture at various heptane concentrations.



**Figure H3** Rate of asphaltene deposition as a function of concentration of unstable asphaltenes obtained from centrifugation of aged oil-heptane mixture at various heptane concentrations.



**Table H1** Data of Asphaltene Deposition Experiment of Effect of Concentration of Unstable Asphaltenes Obtained from Aged Oil-Heptane Mixture

Heptane Concentration (%)	Time of centrifugation (min)	(gasphaltenes/gmixture) (remaining in supernatant)	Density of mixture (kg/m <sup>3</sup> )	Rate of deposition (g/m <sup>2</sup> /day)	Slope of the plots from H3	Diffisivity calculated using slope (m <sup>2</sup> /s)
30.50	0	0.0187	799.37	70.96	3.00E-09	4.2918E-11
30.50	10	0.0176	799.37	36.23		
30.50	30	0.0171	799.37	11.53		
30.51	50	0.0161	799.37	5.02		
29.01	0	0.0180	801.85	19.25	2.00E-09	2.33978E-11
29.01	50	0.0167	801.85	2.45		
28.01	0	0.0190	803.46	13.00	1.00E-09	8.28065E-12
28.01	50	0.0178	803.46	0.00		

**Table H2** Data of Asphaltene Deposition Experiment of Effect of Concentration of Unstable Asphaltenes Obtained from Fresh Oil-Heptane Mixture

Heptane Concentration (%)	Time of centrifugation (min)	(gasphaltenes/gmixture) (remaining in supernatant)	Density of mixture (kg/m <sup>3</sup> )	Rate of deposition (g/m <sup>2</sup> /day)	Slope of the plots from H2	Diffisivity calculated uing slope (m <sup>2</sup> /s)
30.50	0	0.0187	799.37	70.96	3.00E-09	4.2918E-11
30.50	10	0.0176	799.37	36.23		
30.50	30	0.0171	799.37	11.53		
30.51	50	0.0161	799.37	5.02		
29.01	0	0.0180	801.85	19.25	2.00E-09	2.33978E-11
29.01	50	0.0167	801.85	2.45		
28.01	0	0.0190	803.46	13.00	1.00E-09	8.28065E-12
28.01	50	0.0178	803.46	0.00		

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1. Kimchhay L., Vilas Bôas Fávero C., Malakul P., and Fogler H. S. (2017, May 23<sup>rd</sup>) Effects of bead size and concentration of unstable asphaltenes obtained from different centrifugation techniques on asphaltene deposition in packed bed apparatus. Proceedings of the 8<sup>th</sup> Research Symposium on Petrochemical and Material Technology and the 23<sup>rd</sup> PPC Symposium on Petroleum, Petrochemicals and Polymers, Bangkok, Thailand.