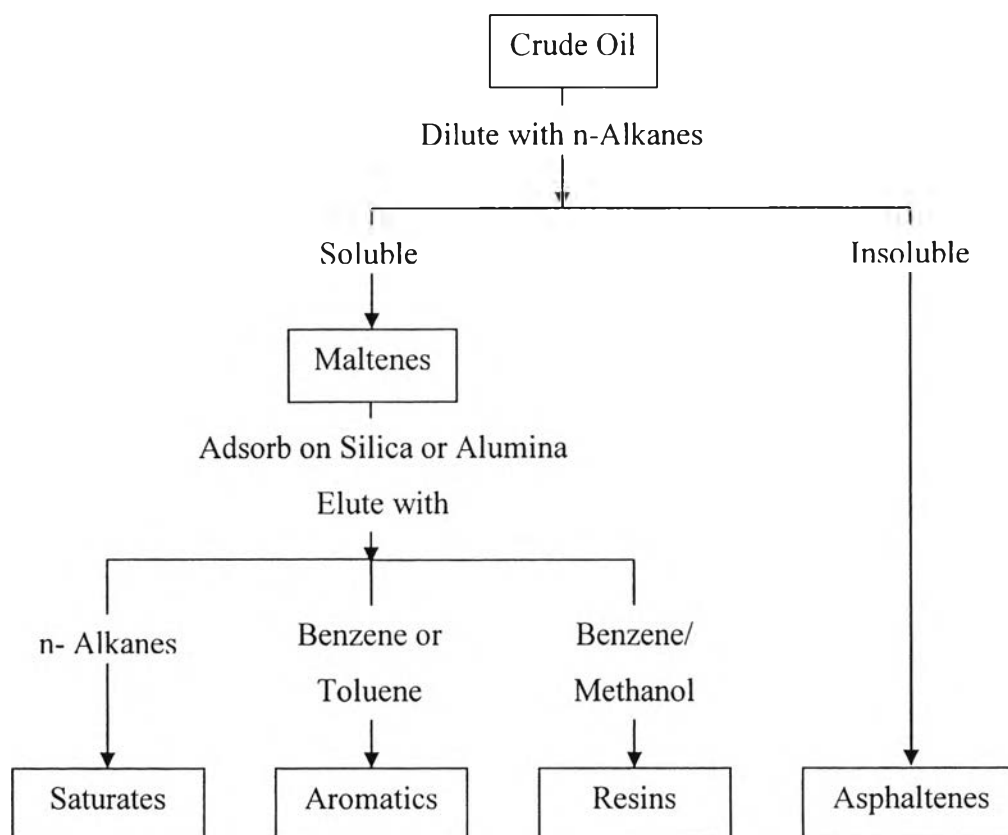




## CHAPTER II LITERATURE REVIEW

### 2.1 Crude Oil

Petroleum crude oil is a complex mixture of hydrocarbons containing variety of molecules with different physical and chemical properties. Commonly the crude oils are separated into four classes of solubility: saturates aromatics, resins, and asphaltenes (SARA) (Wattana, (2004). The schematic of SARA separation is shown in Figure 2.1.



**Figure 2.1** Schematic of crude oil separation (SARA) into four classes of solubility: saturates, aromatics, resins and asphaltenes (Wattana, 2004).

## 2.2 Asphaltenes

Asphaltenes are operationally defined as a solubility class, namely the fraction of crude oil that is insoluble in normal alkanes but are soluble in aromatic solvents. They are dark brown to black dry powders with no definite melting point (Mullin, 2007). In addition, their amounts and properties can be classified by the type of precipitant used, for example, asphaltenes precipitated from crude oil with heptane would be referred as C7-asphaltenes. One method that is used to yield the amount of asphaltene in a given crude oil is the ASTM D2007-80 (1980), where crude oil is diluted by either n-pentane or n-heptane at a volume ratio of 1:40 and then filtered after two days to separate the asphaltenes. The main components of asphaltenes are carbon and hydrogen, but they also contain small quantities of heteroatoms such as nitrogen, sulfur and oxygen and some metals like nickel, vanadium and iron (Kaminski *et al.*, 2000).

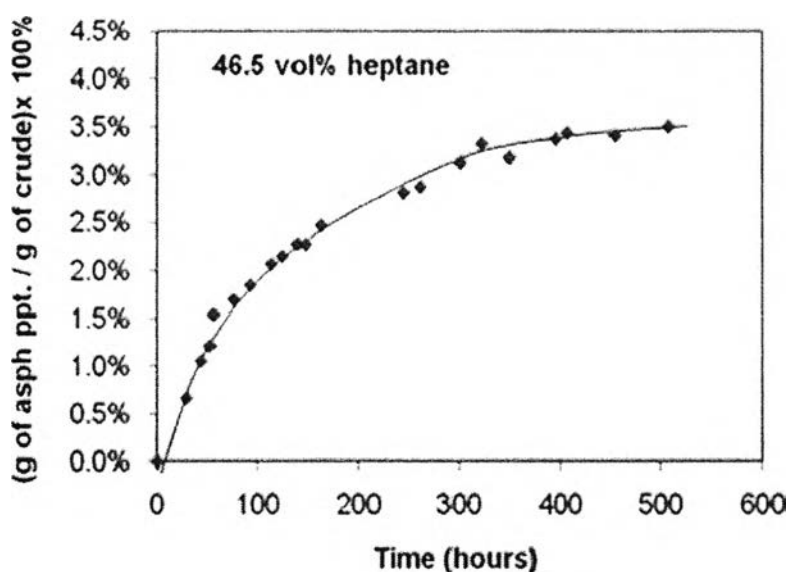
## 2.3 Asphaltene Precipitation Onset Point

Crude oils have been in the reservoirs for millions of years and they exist as a stable mixture at reservoir conditions. A change in thermodynamic conditions, such as pressure, temperature or composition may cause destabilization of the crude oil and asphaltenes can then precipitate out. In field conditions, the most common mechanism for asphaltene precipitation and deposition is a change of pressure during movement of oil from wellbore to the surface (Haskett *et al.*, 1965). The use of an n-alkane precipitant in the laboratory can simulate the destabilization effect of depressurization that occurs in the reservoir (Gonzalez *et al.*, 2007).

Maqbool *et al.* (2009) have shown in that kinetics play a role in asphaltenes precipitation. As can be seen in their article, precipitation does occur for concentrations below the onset volume, but it takes long times, days or months, to be able detect the precipitation. A novel centrifugation-based separation technique was developed to quantify the amount of asphaltenes precipitated as a function of time.

Figure 2.2 has been extracted from Maqbool *et al.* (2009). In this experiment, the amount of asphaltene in a mixture of 46.5 vol% of heptane in K1

crude oil has been investigated as a function of time using the centrifugation technique. It can be seen that the amount of asphaltenes precipitated gradually increases and reaches a plateau value after more than 500 hours. This plateau value corresponds to the equilibrium amount of asphaltenes that precipitate from a mixture of 46.5 vol% heptane in K1 crude oil. Maqbool *et al.* (2009) have also shown that as the heptane concentration increases, the equilibrium amount of asphaltenes precipitated also increases while the time to reach equilibrium decreases. This observation emphasizes the importance of conducting asphaltene precipitation experiments on a longer time scale in order to determine the equilibrium amount of asphaltenes precipitated.



**Figure 2.2** Amount of asphaltenes precipitated as a function of time using K1 crude oil at 46.5 vol% heptane. (Maqbool *et al.*, 2009).

The experimental work present here will focus on capillary deposition experiments, which is one possible approach to detect the instability of asphaltenes more quickly than batch aggregation process due to continuous source of destabilized asphaltenes at the capillary entrance.

## 2.4 Asphaltene Deposition Experiment

In previous capillary deposition works, only the asphaltene deposition near and past the onset point has been largely investigated (Wang *et al.*, 2004; Maqbool *et al.*, 2006). Wang *et al.* (2004) studied the uniformity of asphaltene deposition in capillaries by collecting the deposits and determining the total mass of the deposit. In these experiments, oil-precipitant mixtures were fed into a capillary at a low flow rate of 4.8 mL/h. To ensure proper mixing, the solution flowed through a sonicating bath before entering the capillary. The pressure drop across the capillary was also measured in this work. Nitrogen gas (N<sub>2</sub>) was used to displace the remaining oil in the capillary at a low flow rate and then used to dry the deposit with a high flow rate. The deposit was dissolved with toluene and THF and weighed after the solvent had evaporated. According to Hagen-Poiseuille equation, the pressure drop for a fluid flowing through a capillary tube with radius R and length L is

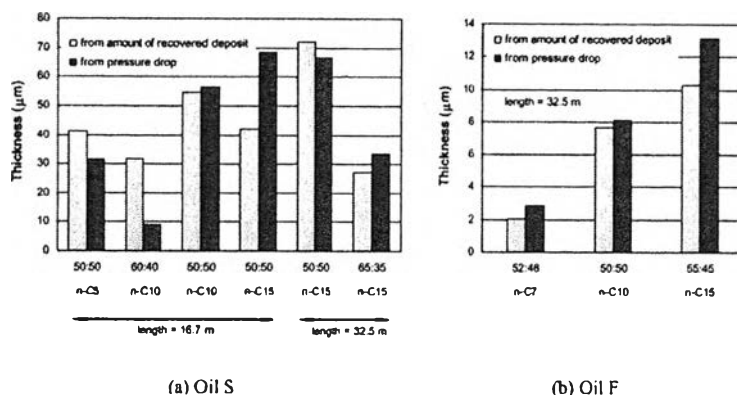
$$\Delta P = \frac{8\mu Q L}{\pi R^4} \quad (1)$$

where  $\mu$  is viscosity and Q is volumetric flow rate.

For the assumption of uniform deposit, the inner surface of the capillary with thickness  $\Delta R(t)$ , the pressure drop  $\Delta P(t)$  will change with time (t) as:

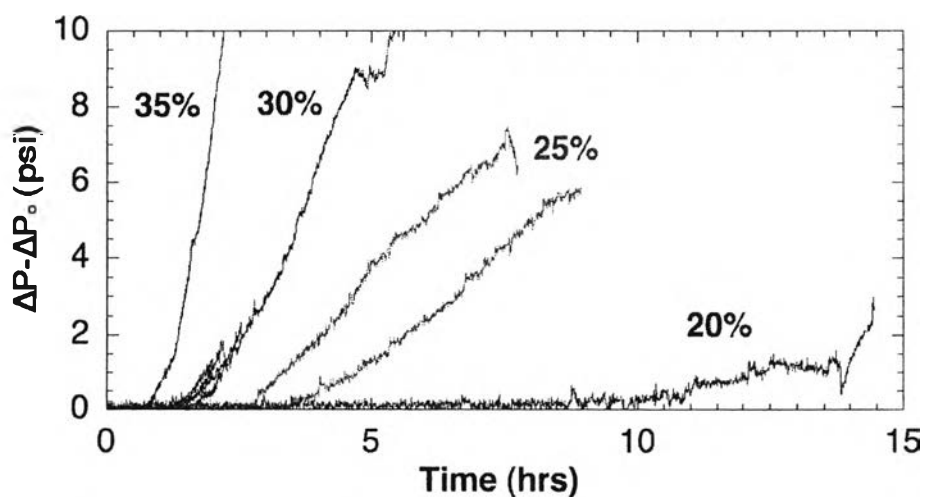
$$\Delta P(t) = \frac{8\mu Q}{\pi} \frac{L}{[R_0 - \Delta R(t)]^4} \quad (2)$$

The author has concluded in this work that the deposit is uniform when the concentration is close to the onset point. The collected deposit is approximately the same as calculated, and the authors considered the deposit as uniform, as can be seen in Figure 2.3.



**Figure 2.3** The thickness from predicted and collected of two crude oils, Oil S and Oil F (Wang *et al.*, 2004).

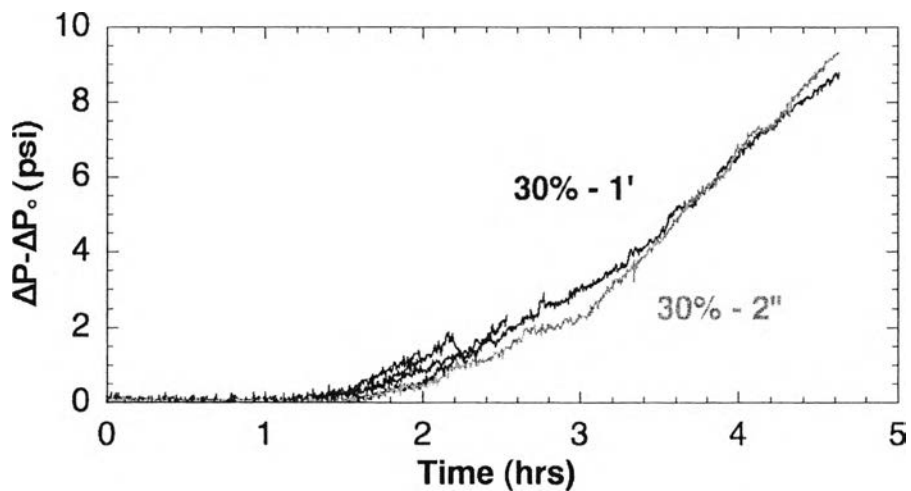
Hoepfner (2010) investigated asphaltene deposition below the onset point. The onset volume of the oil used was 40 vol.% heptane. The measured increase in the pressure drop across the capillary section indicates the formation of deposit inside the capillary. The results reveal that asphaltenes are destabilized and have the ability to deposit before the instability can be identified by microscopy. Figure 2.4 shows the pressure drop profile of different precipitant concentrations and deposition was detected at heptane concentrations as low as 20 vol.%.



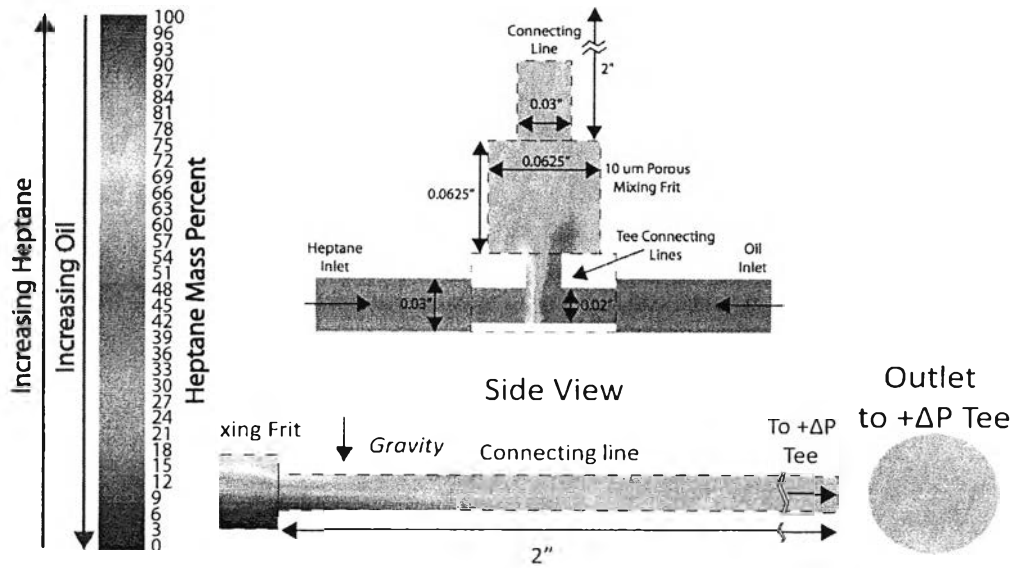
**Figure 2.4** Pressure drop profile of different precipitant concentration (Hoepfner, 2011).

Another conclusion from this work was that deposit is non-uniform and located near the entrance of the capillary. Figure 2.5 shows a comparison between a 1 foot and a 2 inch length from this work indicated that deposit is occurring preferentially near the capillary inlet.

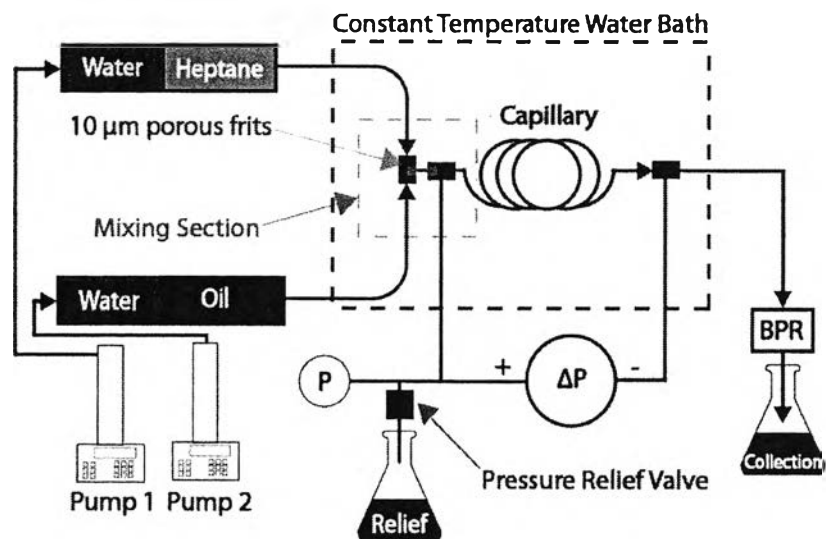
As heptane and crude oil are continuously feed into the capillary, it is mandatory to know whether or not the liquids are being well mixed. In order to obtain to ensure the good mixing, a pre mixing section is used. To validate the proper mixing in the system, Hoepfner (2010) used Computational fluid dynamic (CFD) simulations to demonstrate that the oil:heptane mixture will be well mixed if mixing frit and a 2-inch stainless steel capillary with a 0.03 inch inner diameter (ID) were added before the solution flows into the capillary test section. Figure 2.6 shows the CFD simulations of the mixing system. A pre-filter was also added to prevent asphaltenes formed in the mixing section from travelling into the capillary test section. Figure 2.7 shows the apparatus from this work.



**Figure 2.5** Comparison of  $\Delta P - \Delta P_0$  vs. time plot for the short (2 inch) and long (1 foot) capillaries (Hoepfner, 2011).



**Figure 2.6** Top and side view of the CFD simulations of the mixing system. By the time the mixture reaches the outlet, it is completely mixed (Hoepfner, 2010).

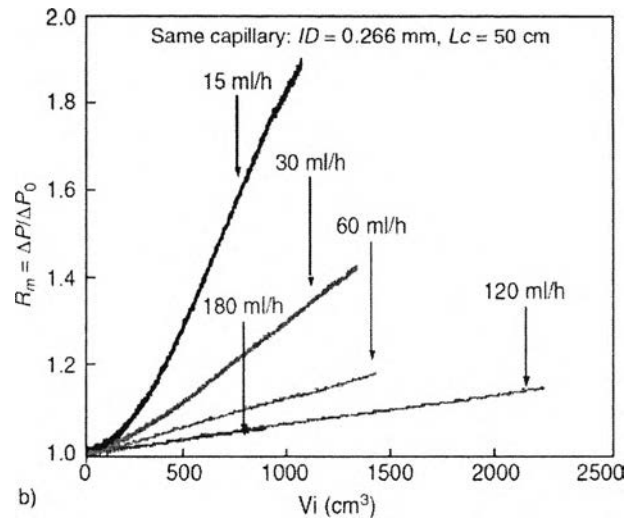


**Figure 2.7** Asphaltene deposition apparatus setup (Hoepfner, 2011).

## 2.5 Effects on Asphaltene Deposition

Nabzar *et al.* (2008) mixed an asphaltene:toluene solution with heptane to study the shear effects on asphaltene deposition by using the same capillary and

varying the shear rate. A sample result is shown in Figure 2.9. The conclusion was that asphaltene deposition is sensitive to the shear rate until it reached a critical shear rate.



**Figure 2.8** Evidence of shear limitation from experiments (Nabzar *et al.*, 2008).

Asphaltene deposition has been investigated in previous studies, but the mechanism is still unknown. To investigate the mechanism of asphaltene deposition, it is important to validate the apparatus and conduct the experiments to verify the proposed mechanism.

The experimental work presented here will focus on studying asphaltene deposition in a capillary at low heptane concentrations, obtaining images of the deposit and evaluating the deposition thickness along the length. Further goals were to determine the quality of mixing in the capillary deposition apparatus, the location of the deposit and the mechanism of asphaltene deposition. Additionally, the deposition behaviour of different types of crude oil was investigated to check for applicability of the results in different reservoirs.