

CHAPTER II LITERARURE REVIEW

2.1 Petroleum Crude Oil

Crude oils are complex mixtures of hydrocarbons containing a variety of components with different physical and chemical properties. Often these components are divided into four major fractions; saturates, aromatics, resins, and asphaltenes (SARA). The SARA separation is based on the difference in solubility and polarity of each fraction as demonstrated in Figure 2.1 (Wattana, 2004).

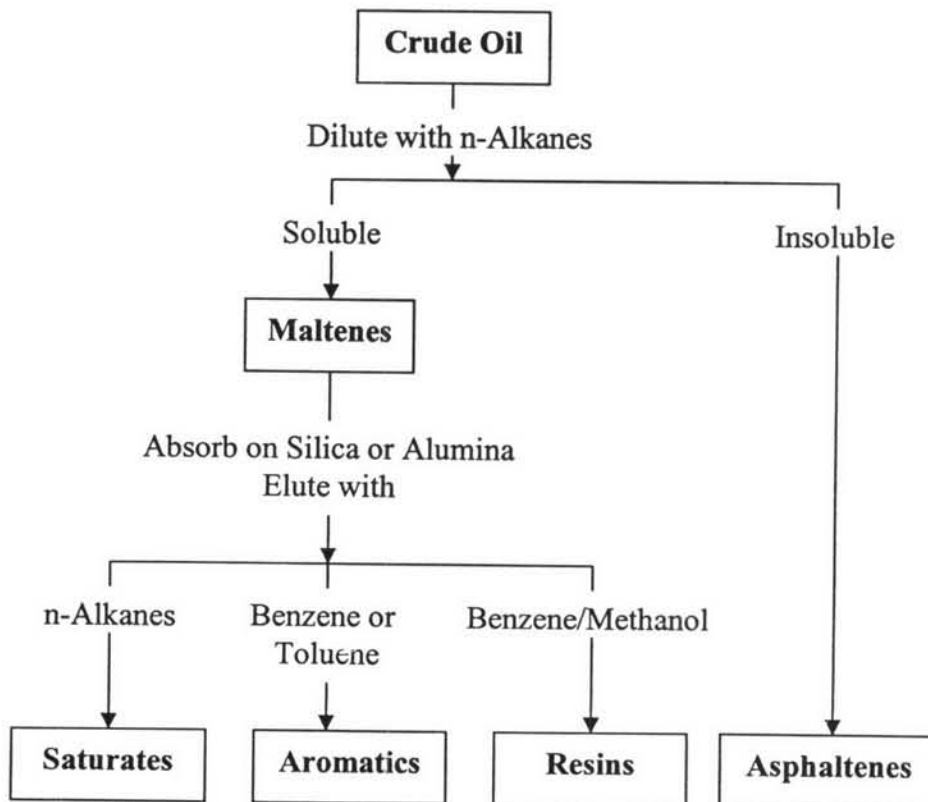


Figure 2.1 Schematic of SARA separation (Wattana, 2004).

2.2 Asphaltenes

Asphaltenes are considered to be one of the most problematic and the least understood organic deposits (Wattana, 2004). Operationally defined on the basis of solubility, asphaltenes are the components of crude oils that are soluble in aromatics such as benzene and toluene, but are insoluble in light aliphatics such as pentane and heptane (Bestougeff and Byramjee 1994; Speight 1999). They are the most polar and heaviest component of crude oils.

Asphaltenes are precipitated from crude oils by adding n-alkane solvents, such as n-pentane or n-heptane, in a volume ratio of at least 1:40 (oil : precipitant). They are dark brown to black friable solids with no definite melting point. In addition to the classical definition, asphaltenes tend to be classified by the particular alkanes used to precipitate them. Thus, there are pentane asphaltenes, hexane asphaltenes and heptane asphaltenes. However, as the size of the precipitating n-alkane molecule decreases, the amount of asphaltene precipitated increases as shown in Figure 1 (Speight 1999). The difference in the amount of asphaltene precipitated by different precipitants, indicates a difference in composition and molecular weight among different n-alkane asphaltenes.

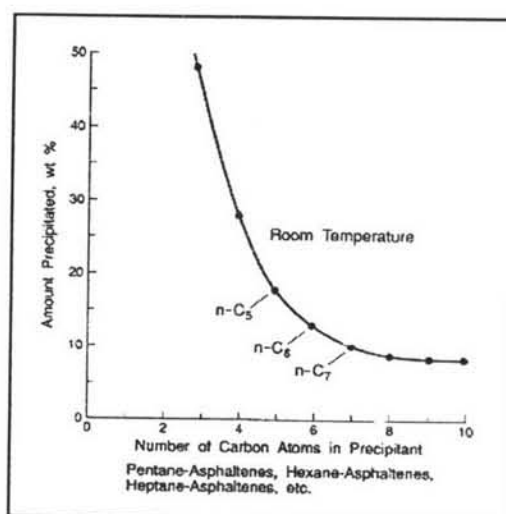


Figure 2.2 Asphaltene yield as a function of the carbon number of n-alkane precipitant (Speight 1999).

2.3 Study of Asphaltene Precipitation Using Refractive Index Measurement

Wattana *et al.* (2003) developed a technique based on the refractive index measurement to monitor the precipitation process and the stability of asphaltenes in crude oil. For a mixture in which there is no significant change of volume after mixing, the refractive index function of the mixture, $f(n) = (n^2 - 1) / (n^2 + 2)$, is equal to the sum of the refractive index functions of each individual component times its volume fraction (φ_i):

$$f(n) = \sum_i \varphi_i f_i(n) \quad (2.1)$$

$$\left(\frac{n^2 - 1}{n^2 + 2} \right) = \sum_i \varphi_i \left(\frac{n^2 - 1}{n^2 + 2} \right)_i \quad (2.2)$$

where n is the refractive index of the substance.

Thus for a pseudo binary mixture, a linear relationship exists between the refractive index function and the volumetric fraction of the components. When crude oil is titrated with a precipitant, a point is reached when asphaltenes start to precipitate out from the solution of crude and precipitant. Asphaltenes are highly refractory components of the crude oil. When they precipitate out, they do not contribute to the refractive index of the solution and a decrease in the refractive index of the solution is observed. Therefore, the onset of asphaltene precipitation is detected from the deviation of refractive index behavior from linearity (Wattana, 2004).

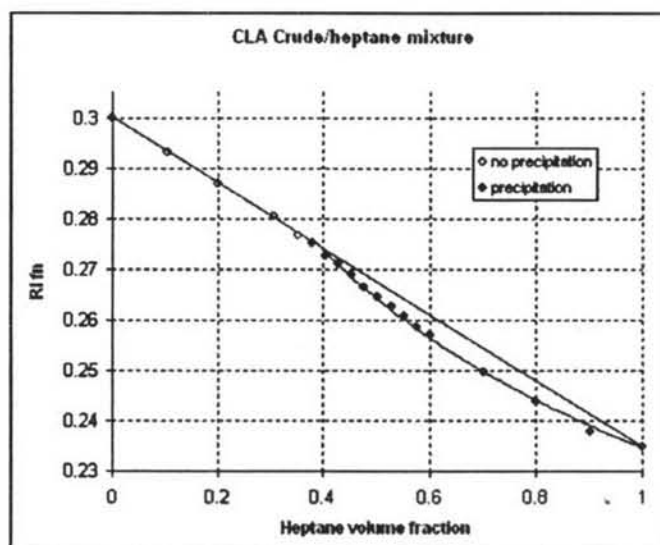


Figure 2.3 Determination of asphaltene precipitation onset point by refractive index technique (Wattana, 2004).

Further work by Wattana *et al.* (2005) showed that the stability of crude oil did not depend on the amount of asphaltenes present, but in fact was dependent on the characteristic nature of the asphaltenes. The distribution of the polar fractions of asphaltenes showed that the asphaltene samples from unstable sources have a substantially greater portion of the higher polar fractions when compared to the asphaltene samples from stable sources. The determination of average molecular weight of asphaltene polar fractions showed that the asphaltene fractions with higher polarity have higher average molecular weight. The polarity and average molecular weight of the asphaltenes were shown to be the dominating factors on the aggregation tendency and stability of asphaltenes in crude oils. However, the technique used can only detect asphaltene precipitation if the asphaltene content of crude oil was high, because techniques like refractive index are based on bulk flocculation.

2.4 Capillary Flow Technique to Study Asphaltene Deposition

Broseta et al. (2000) used pressure drop measurements across a capillary tube to measure the onset of asphaltene deposition. In these experiments, crude oil, solvent and precipitant were injected into a capillary at a constant rate and the pressure drop across the capillary was measured. The pressure drop for laminar flow in a capillary of length L (m), for flow rate Q (ml/min) is given by the Hagen-Poiseuille equation:

$$\Delta P = \frac{8\eta}{\pi r^4} LQ \quad (2.3)$$

where η is the liquid viscosity (cP) and r is the radius of the capillary (m)

Figure 2.4 shows the results for deposition experiments with crude oil B. A ternary mixture of crude oil B, heptane and xylene was injected into the capillary at a constant flow rate and at specified conditions of temperature, pressure and composition. Keeping the flow rate of crude oil and total flow at constant values, the flow of heptane was increased while decreasing the flow rate of xylene at times 1, 2 and 3 in Figure 2.4.

After times 1 and 2 the pressure drop reached a steady value with fluctuations less than 1% of the measurement scale. The slight decrease in pressure drop (or viscosity) with increasing heptane content (or decreasing xylene content) reflects the fact that heptane is slightly less viscous than xylene. When the conditions for deposition were met after time 3, the pressure drop across the capillary tube was no longer constant, but increased with time as a result of the buildup of a deposition layer on the tube walls.

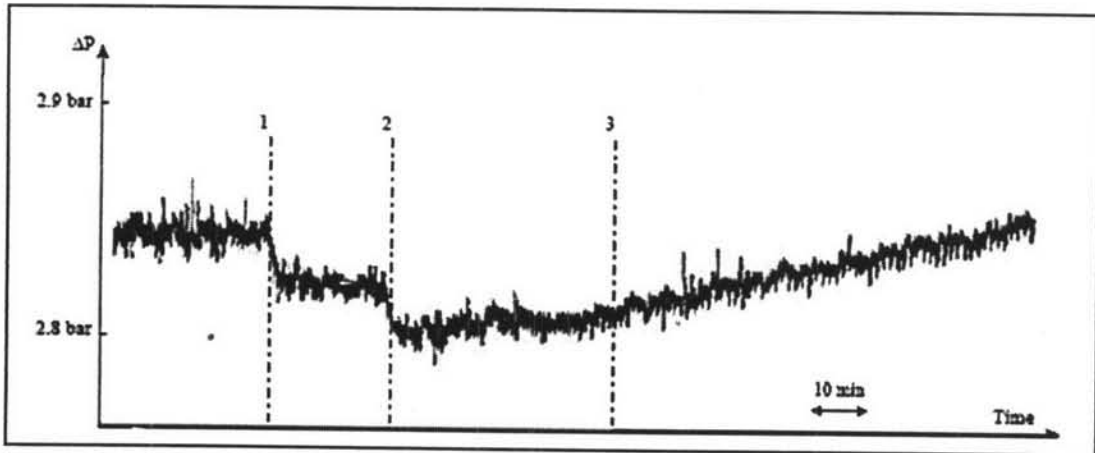


Figure 2.4 Pressure drop evolution for four different crude oil B/xylene/heptane mixtures flowing at $Q=3$ ml/min. The mixtures contained 16.6 vol.% of crude oil B and proportions of flocculent (heptane) that increased from 73.4 to 76.4% (at time 1), then to 79.4% (at time 2) and then to 80.5% (at time 3).

Using the capillary deposition technique, the authors developed asphaltene deposition envelopes for two different crude oils by marking the compositions where asphaltenes would deposit and where they would be stable. They further conducted experiments for bulk flocculation of asphaltenes using conventional light transmission technique. The measured deposition points coincided with bulk flocculation thresholds determined by the light transmission method. However, the light transmission method was difficult for crudes with very low asphaltene content, whereas the capillary deposition method was effective for crudes containing as low as 0.04 wt. % asphaltenes. Further, the capillary flow technique was found to be extremely sensitive to the deposition onto the capillary walls. The study did not discuss the effect of different precipitants on asphaltene deposition, which is an important factor for the study of asphaltene precipitation and deposition as discussed in section 2.2.

2.5 Subsequent Studies in Asphaltene Deposition

Wang *et al.* (2004) used a similar technique as Broseta *et al.* (2000) to study the influence of factors including temperature, degree of asphaltene instability, and precipitant types on asphaltene deposition for mixtures of stock-tank oils and n-alkanes. The experiments were carried out over a temperature range of 20⁰C to 60⁰C. In the experiments, pressure drop across the capillary tube was used to estimate the amount and distribution of deposit formation. For the experimental runs below the wax appearance temperature, intermittent pressure spikes were observed indicating the deposition of wax. Above the wax appearance temperature, deposition occurred gradually from near-onset mixtures created by co-injection of oil and n-alkane precipitants. Examination of the deposited material that was collected after the experiments showed that it contained not only asphaltenes but also waxes.

Much different depositional characteristics were observed for solutions of asphaltenes in an aromatic solvent than for the stock-tank oil from which they were derived. Existing asphaltic particles in stock-tank oil samples did not create deposits, but this phenomenon could not be explained. Figure 2.5 shows the results for asphaltene deposition tests. As shown in the figure, asphaltenes flocculated by addition of longer chain n-alkanes deposited more material than those flocculated by shorter chain n-alkanes. However, this result is not in agreement to the asphaltene precipitation results shown in Figure 2.2 (Speight, 1999) where longer chain n-alkanes have been demonstrated to precipitate lesser amount of asphaltenes. It is possible that the deposition observed by Wang *et al.* (2004) was influenced by the wax present in crude oils. Hence, no concrete conclusions can be made about the effect of different precipitants on the deposition of asphaltenes.

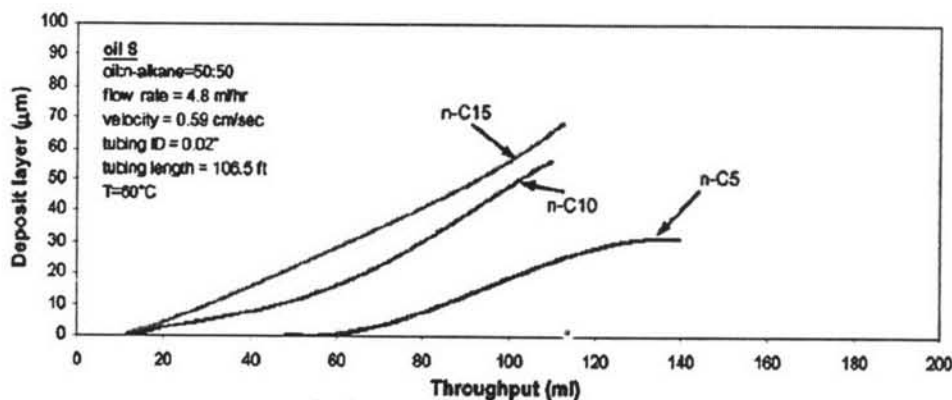


Figure 2.5 Rates of deposit formation for mixtures of oil S with n-pentane (n-C5), n-decane (n-C10), and n-pentadecane (n-C15) (Wang *et al.*, 2004).

Moreover, the experimental technique used by Wang *et al.* (2004), as shown in Figure 2.6, may not be able to capture the entire effect of asphaltene deposition. As discussed in their work, existing asphaltene particles in stock-tank oil samples did not create deposits. Based on this fact, the asphaltene particles that precipitate out in the connecting tubing between the mixing node and the capillary entrance during deposition experiments should not deposit. Hence, the deposition results would not be completely representative of the crude oil as a part of the precipitating asphaltenes may not be able to contribute to the deposition results.

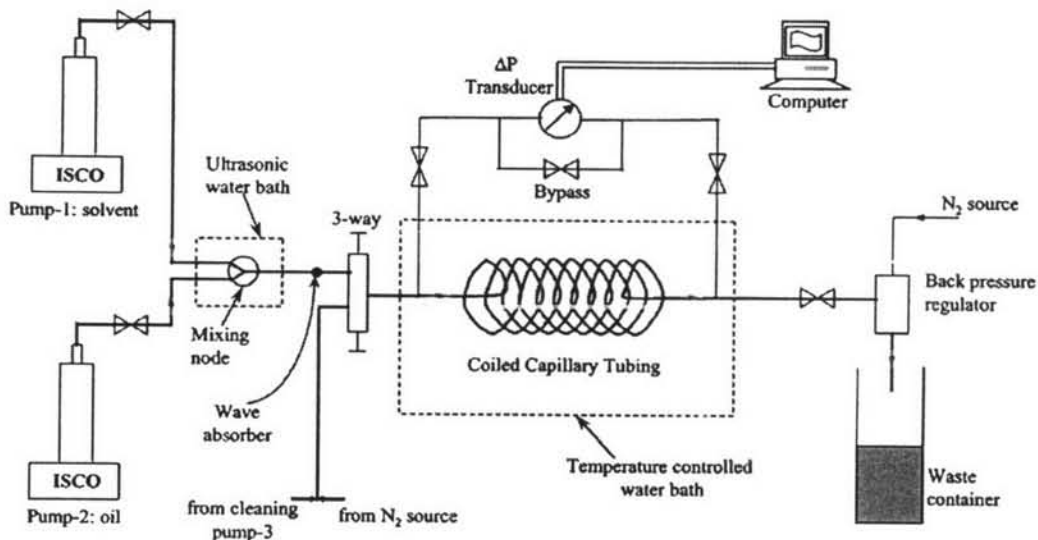


Figure 2.6 Schematic view of deposition test apparatus (Wang *et al.*, 2004).

The aim of this research is to develop an improved technique to investigate asphaltene deposition by building on the work of Broseta *et al.* (2000) and Wang *et al.* (2004). By using a wax-free crude oil, the potential effects of wax on deposition are eliminated, allowing for the deposition of solely asphaltenes to be examined.