CHAPTER II

LITERATURE REVIEW

2.1 Asphaltenes

Asphaltenesare defined as the heaviest and most complex fraction of crude oil. They are composed of condensed polynuclear aromatics and contains small amounts of heteroatoms (S, N, and O), and trace amount of nickel and vanadium (Ancheyta et al., 2001). Asphaltene molecules are believed to have fused aromatic ring clusters with varying lengths of alkyl side chains attached to the aromatic cores. Four of the proposed asphaltene structures are illustrated in Fig.2.1.1.
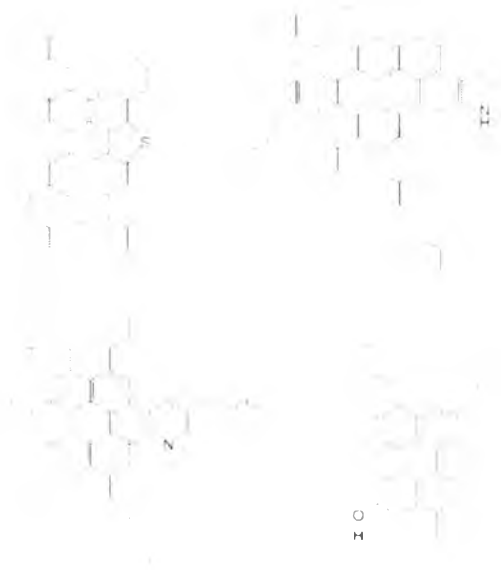

Figure 2.1.1 Hypothetical asphaltene structures (Mullins, 2010).

They are also defined as a solubility class consisting of compounds in crude oils that precipitate upon the addition of n-alkanes. To ensure complete precipitation of total asphaltenes, an n-alkane/crude oil ratio of 40:1 is often used. This is the ASTM D3279 standard procedure (Pillon L. Z., 2001). The precipitants used to precipitate asphaltene classify asphaltene types; for example, asphaltenes precipitated by addition of pentane will be called pentane asphaltenes.

2.2 Asphaltene precipitation

Asphaltenes are materials that get destabilized when there are changes in temperature, pressure and oil composition. The destabilization of asphaltenes results in precipitation and deposition in oil production pipelines and block pore spaces, causing severe economic losses in the petroleum industry.

To better understand the deposition mechanism, one needs to first know how asphaltenes aggregate and form precipitates that could deposit in pipelines. Spiecker et al. (2003) studied the aggregation and solubility behavior of asphaltenes and their subfractions. They investigated using four types of crude oils and fractionated them in mixtures of heptane and toluene. Vapor Pressure Osmometry (VPO) and Small Angle Neutron Scattering were used to chemically analyze the sub-fractions. Fossen et al. precipitated asphaltenes using a two-step precipitation procedure in 2006. They precipitated two fractions of asphaltene called first fraction with volume ratio of n-pentane/crude oil of 3:1 and second fraction with 18:1 volume ratio of n-pentane/crude oil from three different types of crude oils. The whole fraction of asphaltene was precipitated using 40:1 n-pentane/crude oil volume ratio. They found that the amount of asphaltene precipitated were larger as compared to earlier precipitations on the same crude oil using hexane. They also found that different fractions of asphaltenes, when dissolved in a solvent, give different solvent properties and that the asphaltenes should be looked at as more than one solubility class. They performed SANS measurements to determine the aggregate size by using the Guinier approximation and obtaining R_g (radius of gyration). The results showed that the first fraction formed larger aggregates than the second fraction for all the three types of crude oil investigated.

Previous work by Maqbool et al. (2009) investigated the kinetics of asphaltene precipitation from crude oils using n-alkane precipitant. They found that asphaltene precipitation is a time-dependent process from microscopy and centrifugation experiments and the precipitation onset time increases exponentially by decreasing heptane concentration. Additionally, there is no single concentration which can be identified as the critical precipitant concentration. They were able to establish the solubility of asphaltenes as a function of precipitant concentration. They had also done another work studying the effect of temperature on the precipitation kinetics of asphaltenes (Maqbool et al., 2010). The results showed that three factors that were greatly affected by temperature are solubility of asphaltenes, variation in liquid composition due to heating and role of viscosity on the rate of aggregation. Solubility of asphaltenes increases with increasing temperature and consequently a smaller mass of asphaltenes will precipitate indicating that at higher temperature, most asphaltenes are soluble.

Other factors such as hydrocarbon expansion, chemical change in oil due to heating and change in composition due to evaporation play no significant effects on asphaltene precipitation kinetics. However, there is a significant effect of temperature on the viscosity. The change in temperature leads to a change in viscosity which in turn affects the collision kernel for the Brownian flocculation of asphaltenes and controls the onset time for precipitation (Maqbool et al., 2010).

They had also developed a population balance model simulating the asphaltene particles growth from nanometer size to micrometer size. The model is in good agreement with the experimental data for the evolution of asphaltene aggregates at different times collected by centrifugation (Maqbool et al., 2011).It has also been found that the growth in the asphaltene aggregate size increases with increasing heptane concentration.

In 2013, Haji Akbari Balou et al., have developed a unified model for asphaltene aggregation. This model incorporated the asphaltene precipitation detection time (time for the asphaltene nanoaggregate to reach 0.5μm detectable size under the microscope) with the difference between solubility parameter of asphaltene

and solution squared, $(\delta_{asphaltene}-\delta_{solution})^2$ and a master curve for this correlation was generated as shown in Figure 2.1.1.
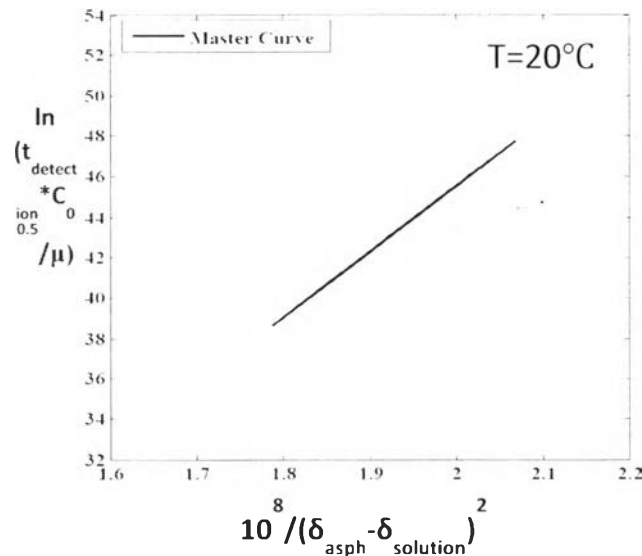

Figure 2.2.1 Master Curve for relation between detection time and the difference between solubility parameter of asphaltene and solution squared at 20°C (Haji Akbari Balou et al., 2013).

This correlation assumes that asphaltene solubility parameter for the same crude oil is constant and the maximum potential barrier, U_{max}, which depends on the overall interaction energy between asphaltenes, is assumed to be inversely proportional to the difference between solubility parameter of asphaltene and solution squared. In order to obtain the detection time for asphaltene precipitation, onset experiment must be performed. Once detection time and solution solubility parameter are known, the model can be used to predict the asphaltene solubility parameter as well as detection time at other heptane concentration. In this work, this model will be incorporated in determining the solubility parameter of the time-based asphaltene fractions to aid in understanding their aggregation behavior.

2.3 Asphaltene characterization

After numerous works done on asphaltene precipitation mechanism, it still remains unclear as to why asphaltenes precipitate at different times. There must be differences in their properties that govern the aggregation and precipitation which cause this phenomenon.

This problem has lead researchers to investigate more deeply into the properties of asphaltene that cause this differences by applying various characterization techniques, for example, carbon Nuclear Magnetic Resonance (^{13}C NMR), proton Nuclear Magnetic Resonance (^{1}H NMR), Fourier Transform Infrared spectrometry (FTIR), Small Angle X-ray Scattering (SAXS), X-ray Diffraction (XRD), Vapor Pressure Osmometry (VPO), Small Angle Neutron Scattering (SANS), Elemental Analysis (EA) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Spiecker et al. studied the aggregation and solubility behavior of asphaltenes and their sub-fractions using VPO and SANS (Spiecker et al., 2003). Less soluble fractions in heptol mixture formed larger aggregates. Furthermore, aggregate size increased with decreasing aromaticity of the solvent used to dissolve asphaltenes. Elemental composition and metal content analysis also showed that the less soluble fraction contained higher metal content but lower H/C ratio. Spiecker et al. also proposed that aggregation is enhanced by aromatic π-bonding interaction due to low H/C ratio and nitrogen content. They concluded that the less soluble asphaltene fractions are the fractions that contributed to aggregation and caused petroleum production problems.

Fossen et al. precipitated two fractions of asphaltenes. The first fraction was extracted with a volume ratio of n-pentane/crude oil of 3:1, and the second fraction was extracted with an 18:1 volume ratio of n-pentane/crude oil (Fossen et al.,2006). Total asphaltenes were precipitated using 40:1 n-pentane/crude oil volume ratio. Three types of crude oils were investigated in their study. It was found that the amount of asphaltene precipitated with heptane was larger as compared to earlier precipitations on the same crude oil using hexane. Fossen et al. characterized their

fractionated asphaltenes using Elemental Analysis, FTIR, proton and carbon NMR spectrometry, NMR- distortionless enhancement by polarization transfer (DEPT) and Laser desorption ionization-mass spectrometry (LDI-MS). They had found that the first fraction (3:1 pentane to crude oil ratio) had larger amounts of heteroatoms than the second fractions and the total asphaltenes. FTIR, NMR and NMR-DEPT showed that the first fraction was more aromatic and had a more polar aromatic core with more rings. Their LDI-MS results showed that the less soluble fraction had higher average molecular weight compared to the other fractions (Fossen et al., 2001). Maqbool et al. studied asphaltene precipitation as a function of precipitant concentration. Dielectric constant measurements, metal content, and polarity-based fractionation were used to characterize asphaltene properties. The first fraction to precipitate showed higher dielectric constant and metal content compared to other fractions (Maqbool et al., 2009).

Aforementioned studies have shown that properties of asphaltenes precipitated at different solvencies (e.g. different precipitant concentration) might be different. However, work done by Maqbool et al. has shown that not only the precipitant concentration is important in controlling precipitation rate of asphaltenes but precipitation rate of asphaltenes is also a strong function of time for a single precipitant concentration. Maqbool et al. showed that: (1) asphaltene precipitation is a time-dependent process as shown from the microscopy images in Figure 2.3.1 and centrifugation plot (Figure 2.3.2), (2) the precipitation onset time increases exponentially with heptane concentration, and (3) there is no single concentration which can be identified as the critical precipitant concentration (Maqbool et al., 2009).
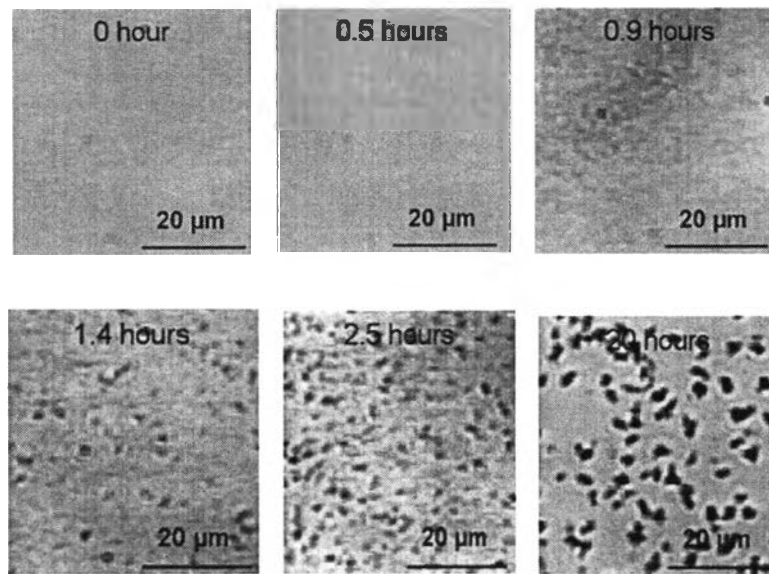
Figure 2.3.1 Micrographs showing the time dependency of asphaltene precipitation for a crude-heptane mixture containing 50 vol% heptane and 50 vol% K1 crude oil (Maqbool et al., 2009).
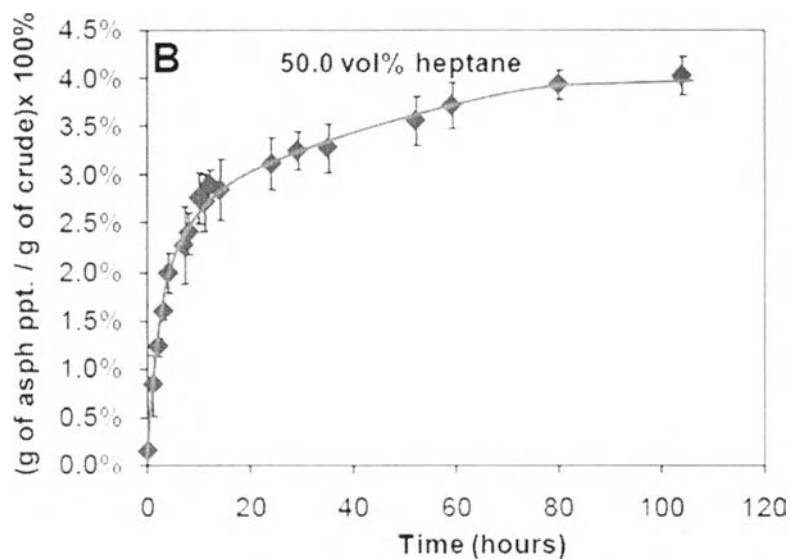

Figure 2.3.2 Amount of asphaltenes precipitated as a function of time for K-1 crude oil at 50 vol% heptane concentration (Maqbool et al., 2009).

It is clear from the centrifugation plot (Figure 2.3.2) that different amounts of asphaltenes are precipitating from solution at different times for a fixed precipitant concentration. This time dependency for amount precipitated can be merely due to

time dependency in aggregation of asphaltenes from nano-scales to micron-scale. However, in addition to kinetic limitations, the properties of aggregating asphaltenes can also play a role in controlling the aggregation rate.

In the work of Maqbool et al., a binary mixture of n-pentane (non-polar) and methylene chloride (polar) was also used to test the polarity of each fraction and found that the first fraction to precipitate was the most polar fraction which is consistent with previous work (Wattana et al., 2005, Maqbool et al., 2009). Additionally, there was no significant difference in the trends observed for the metal content of asphaltene fractions precipitated as a function of concentration and they assumed that there will be a small difference in the properties of asphaltene precipitated as a function of time. However, none of the previous literatures has investigated the influence of asphaltene properties on their aggregation tendency for a fixed precipitant concentration. In order to investigate the importance of asphaltene properties on their aggregation tendency andconsequently their aggregation rate, we have investigated these properties using several characterization techniques and try to correlate the properties of the time based asphaltene fractions with their aggregation behavior from microscopy experiments.