

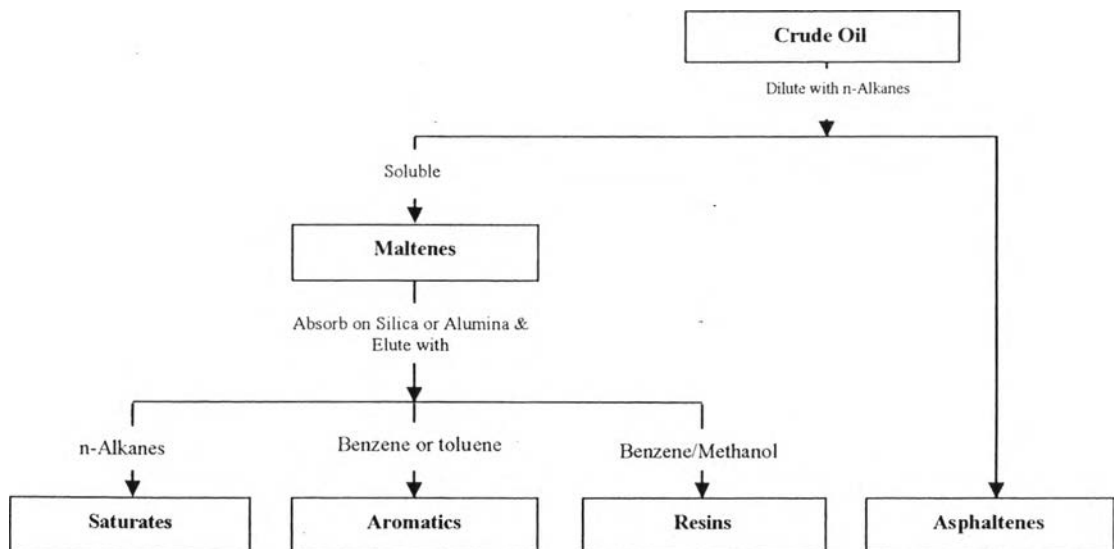
## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Petroleum Crude Oil and Asphaltenes

Crude oil is a mixture of thousands of hydrocarbon compounds ranging in size from the smallest, methane, with only one carbon atom, to large compounds containing 300 and more carbon atoms. A major portion of these compounds consists of paraffins or isomers of paraffins. Most of the remaining hydrocarbon compounds are either cyclic paraffins called naphthenes or dehydrogenated cyclic compounds as the aromatic. There are also present as impurities, small quantities of sulfur, nitrogen and metals (Jones *et al.*, 2006).

The crude oil often divided into four fractions: saturates, aromatics, resins, and asphaltenes by the process called “SARA separation”. The SARA separation is operated on a basis of difference in solubility and polarity of each fraction. Asphaltenes are precipitated from the petroleum crude oil by an addition of an excess of a liquid paraffinic hydrocarbon. The remaining solution obtained as filtrates is called “maltenes”. Saturates, aromatics, and resins in maltenes are then separated with the solid adsorbents and elution with solvents of different polarity. The schematic of SARA separation is shown in Figure 2.1 (Speight *et al.*, 1999).



**Figure 2.1** Schematic of SARA separation (Speight *et al.*, 1999).

Asphaltenes are the heaviest and most complex fraction of petroleum crude oil. They are operationally defined as the fraction which is insoluble in normal heptane (or pentane), but soluble in toluene (Sheu *et al.*, 1995). The physical appearance of asphaltenes is dark brown to black friable solids having no definite melting point and usually foam and swell on heating to leave a carbonaceous residue (Speight *et al.*, 1999). In most researches, asphaltenes are obtained by addition of n-alkanes such as pentane and heptane to crude oil or bitumen and collecting the solids precipitated.

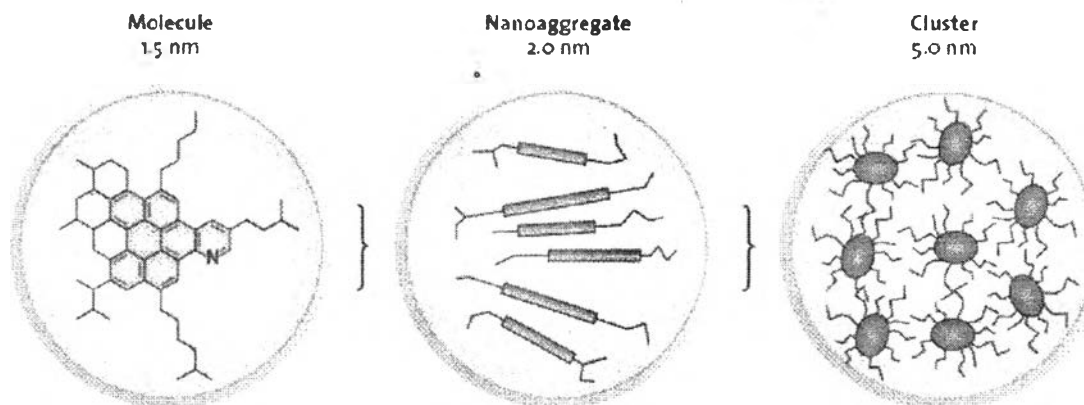
## 2.2 Chemistry and Molecular Nature of Asphaltenes

The composition of asphaltenes depends on the nature of hydrocarbon precipitant and precipitation conditions. Generally, asphaltenes are mainly composed of carbon and hydrogen. They also comprise of polycyclic aromatic hydrocarbons with a random distribution of heteroatoms (e.g., N, S, O) and trace metals (e.g., V, Ni, Fe), which cause a significant impact on the properties of asphaltenes (Mullins *et al.*, 2007).

The molecular structure of asphaltenes has been the subject of numerous investigations, but they are still raven because of the great complexity of the asphaltenes. Many researchers have proposed the possible structure of asphaltenes. An example of proposed molecular structure of asphaltenes is shown in Figure 2.2. The analytical and spectroscopic techniques have shown that asphaltenes are composed of a distribution of highly differentiated and very complex aromatic clusters, surrounded by aliphatic chains and heteroatoms. It has been proposed that asphaltenes consist of aromatic compounds with  $\pi$ - $\pi$  interactions, which undergo acid-base interaction and self-associated through hydrogen bonding (Chang *et al.*, 1994).

A model has been proposed to account for the structural elements of asphaltenes. It specifically accounts for different chemical moieties in asphaltenes such as polycyclic aromatic hydrocarbon (PAHs), PAH stacks, alkane, petroporphyrins. This model has been further modified with some experimental evidences and known as “Modified Yen model” or “Yen-Mullins model” (Mullins *et*

*al.*, 2011). Figure 2.2 shows the structure of asphaltene molecular architecture and aggregates proposed by Yen-Mullins model.



**Figure 2.2** The Yen-Mullins model (Mullins *et al.*, 2012).

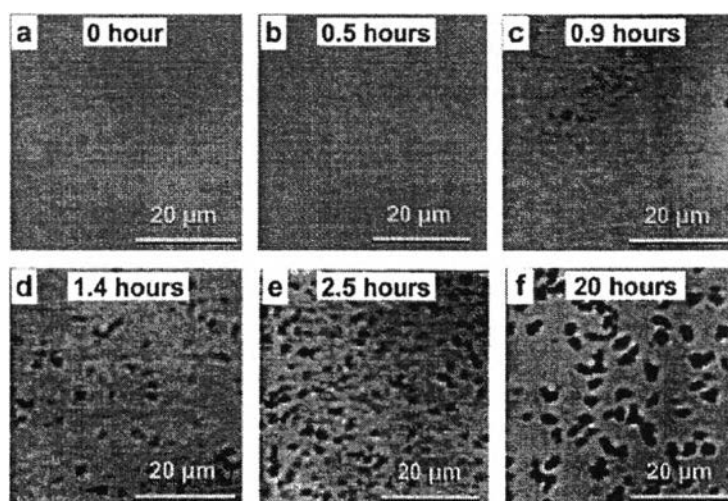
According to Figure 2.2, the predominant asphaltene molecular architecture contains a single, moderately large polycyclic aromatic hydrocarbon with peripheral alkanes, which known as “Island architecture”. Asphaltene molecules form nanoaggregates with aggregation numbers of approximately six, with a single disordered PAH stack. Asphaltene nanoaggregates can form clusters with the aggregation numbers of approximately eight.

It is believed that asphaltenes exist in the crude oil as colloidal suspension and are stabilized by resins. Since resins have high polarity, and attacked by the charged asphaltene kernels, as well as  $\pi$ - $\pi$  orbital associations, they concentrate around the surface of the asphaltene particle forming a protective layer (Leontaritis *et al.*, 1989). Asphaltenes and resins may attach each other to form asphaltene micelle-like aggregates (Chang *et al.*, 1994). However, such micelle-like aggregates can be destroyed. With alterations in temperature, pressure and composition of the crude and injection fluids, which are results of crude oil processing, the colloidal asphaltene molecules were destabilized and start to aggregate, which consequently results in precipitation and flocculation (Branco *et al.*, 2001).

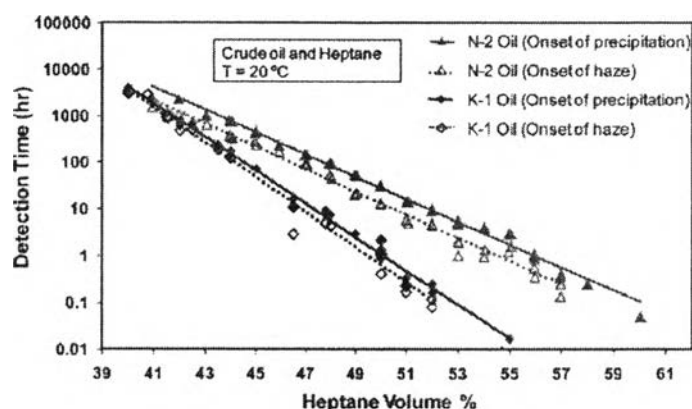
In laboratory, the destabilization of asphaltenes is induced by adding precipitants, usually n-heptane, directly into the crude or model oils.

### 2.3 Kinetics of Asphaltene Aggregation and Role of Soluble Asphaltenes

Asphaltene aggregation is a time-dependent process that can take time from one minute to several months. To investigate the kinetics effect of asphaltene precipitation, a new time-related parameter has been introduced. Maqbool *et al.* (2009) used optical microscopy to study the kinetics of aggregation in microscopic level. They defined the average time between the particle (size~0.5 micron) detection time and haze (cloud of small particles) detection time as “precipitation onset time” or “detection time” and this experiment is called “detection time experiment”. This parameter was used extensively in earlier studies of kinetics of asphaltene aggregation. The longer detection time refers to higher stability of asphaltene in crude oil. An example of micrographs of asphaltene particles observed and detection time experiment results are shown in Figure 2.3 and 2.4, respectively.

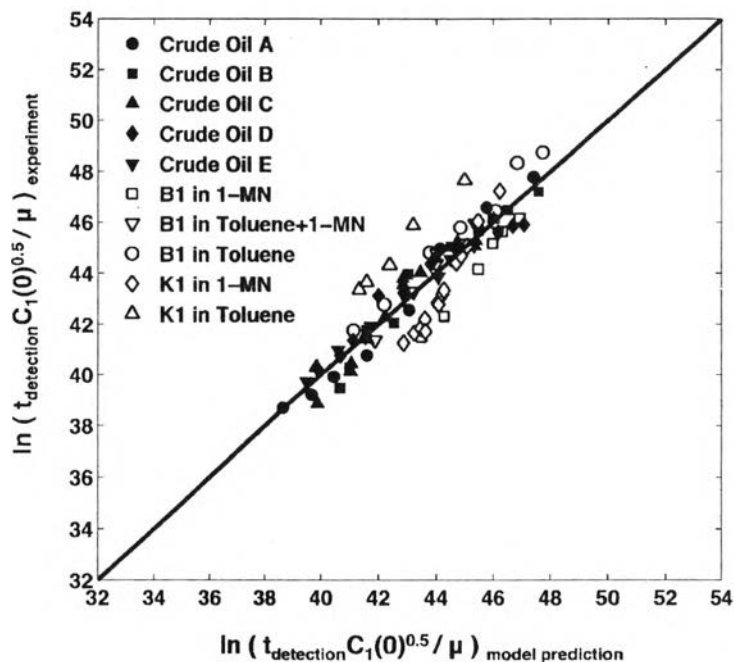


**Figure 2.3** Micrographs show the growth of asphaltene particles after n-heptane addition (Maqbool *et al.*, 2009).



**Figure 2.4** The detection time of Alaskan crude oils (K-1 and N-2) at different heptane concentrations (Maqbool *et al.*, 2009).

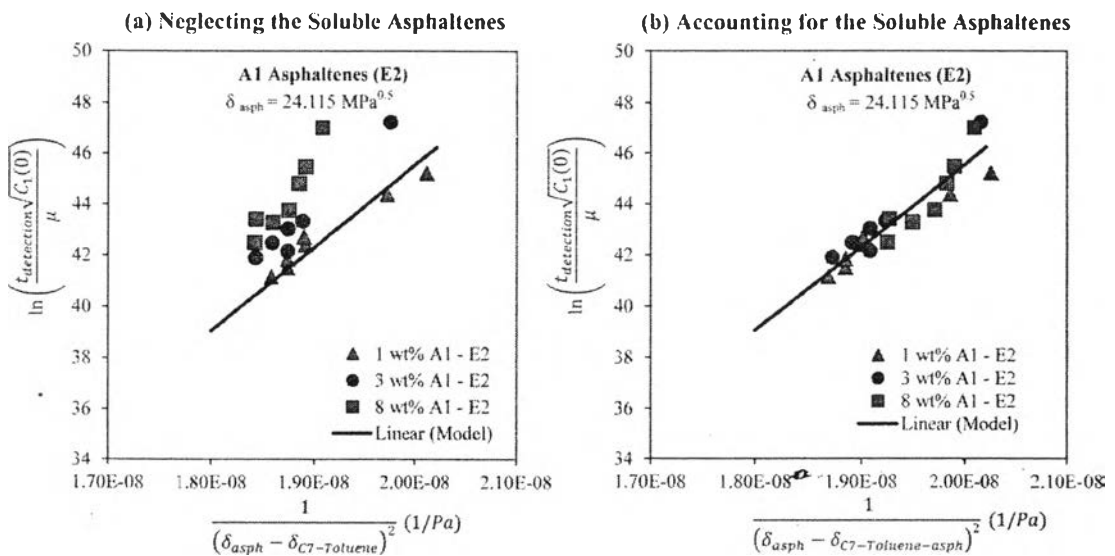
Haji-Akbari *et al.* (2013) has demonstrated that the properties of the crude oil or the solvent used to stabilize asphaltenes (e.g. viscosity and solubility parameter) strongly affect the aggregation rates. By accounting for Smoluchowski's aggregation model (Krapivsky *et al.*, 2010), Flory–Huggins solution theory (Prausnitz *et al.*, 1998), Fuch's stability ratio (Elimelech *et al.*, 1998) and certain key assumptions, the kinetics of precipitation is shown universal among many different crude oils and collapse onto a single master curve as shown in Figure 2.5. This unified model correlates the physical properties of solvent or crude oil (i.e. viscosity and solubility parameter) and the parameters of asphaltene aggregation which are initial concentration, solubility parameter and detection time. This finding leads us to a better understanding of the properties that govern the destabilization and growth processes (Haji-Akbari *et al.*, 2013).



**Figure 2.5** A unified model of asphaltenes precipitation for crude oils and model oils (Haji-Akbari *et al.*, 2013).

Haji-Akbari *et al.* (2014) also studied the effect of asphaltene concentration on their aggregation and precipitation tendencies after their destabilization with heptane for three different types of asphaltenes. It is intuitively expected that any increase in asphaltene concentration will accelerate the precipitation kinetics after heptane addition. They have shown that for asphaltene concentrations below 1 wt % in toluene, this expected trend is indeed experimentally valid. However, for asphaltene concentrations above 1 wt%, an increase in concentration causes to slower aggregation rates. They believe that this counterintuitive decline in the aggregation rate is due to the stabilizing effect of stable or soluble asphaltenes. The differences in aggregation behavior for concentrations below and above 1 wt% are attributed to two competing effects. First, there is an increase in the number of insoluble asphaltenes as the total asphaltene concentration increases, thus leading to an increase in collision frequency. Second, there is an increase in the solvency power of the solution (i.e., the solubility parameter) as a result of an increase in the amount of soluble asphaltenes leading to a decrease in coagulation efficiency. The

aggregation behavior at concentrations below 1 wt% is dictated by the increase in collision frequency, whereas at concentrations above 1 wt%, the rate is controlled by the reduction in coagulation efficiency. They also overlooked this effect in their existing aggregation models (Haji-Akbari *et al.*, 2013) as shown in Figure 2.6. It is shown that without accounting for the effect of soluble asphaltene in solubility parameter of solution, the aggregation rates for high asphaltene concentrations significantly deviate from the curve as shown in Figure 2.6a. However, after taking the effect of soluble asphaltene into account, the trend follows the master curve as shown in Figure 2.6b. This result reveals the role of soluble asphaltene in the aggregation process of asphaltene.



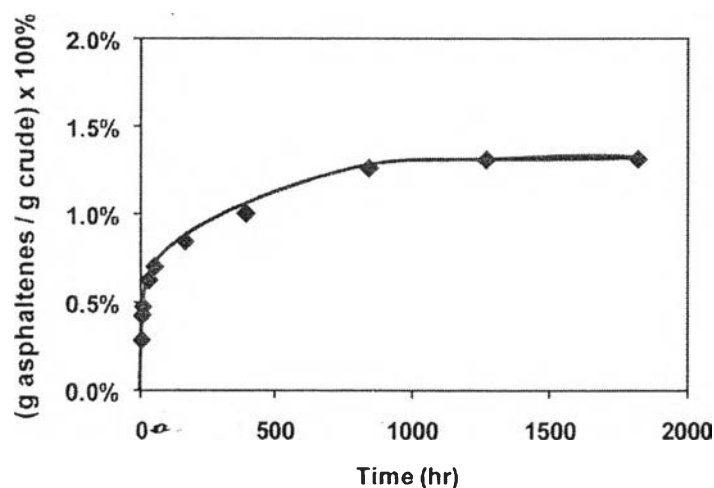
**Figure 2.6** Plot of unified aggregation model for 1, 3, and 8 wt% Arab Medium (AM) asphaltene in toluene with respect to the master curve (a) before accounting for the contribution of soluble asphaltene (b) after accounting for the contribution of soluble asphaltene.

## 2.4 Asphaltene Equilibrium Solubility

After n-alkane addition, some of asphaltene nanoparticles will start to agglomerate and precipitate out of the solution. The asphaltene that precipitates out of the solution is called “insoluble” and the rest that remains in the solution is called

“soluble” asphaltenes. The term “insoluble” and “soluble” are very sensitive, as it heavily depends on the amount of n-alkane precipitant added. For instance, the asphaltenes that is insoluble at higher heptane content will become soluble at lower heptane content. The mass ratio between soluble asphaltenes and total amount of asphaltenes in the system is the solubility of asphaltenes at that condition.

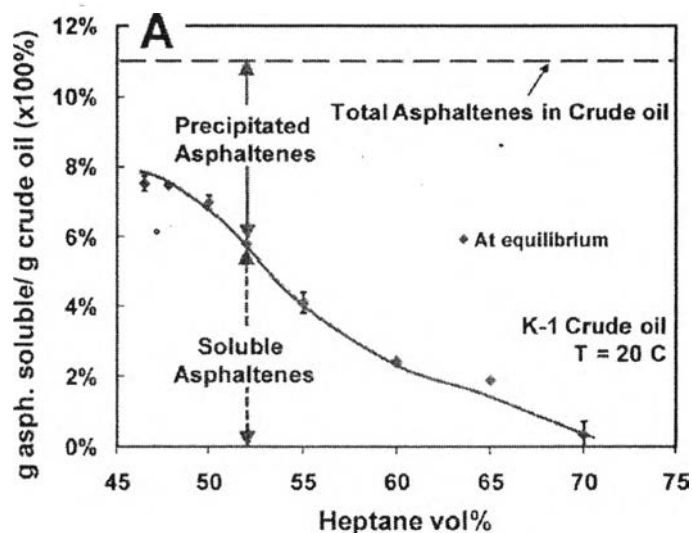
Maqbool *et al.* (2009) had developed a centrifugation-based separation technique to quantify the solubility of asphaltenes in crude oil-heptane mixtures. They found that the amount of insoluble asphaltenes gradually increases over time, as shown in Figure 2.7. The amount of insoluble asphaltenes will increase kinetically until reach a “plateau” value. The asphaltene solubility at the plateau is the thermodynamics solubility of asphaltenes or “equilibrium solubility”.



**Figure 2.7** Amount of asphaltenes precipitated as a function of time for N-2 crude oil at 60 vol% heptane (Maqbool *et al.*, 2009). The value reaches plateau after 800 hours.

The equilibrium solubility of asphaltenes is a function of precipitant concentration. As the precipitant concentration increases, the equilibrium solubility decreases and the time required to reach the equilibrium, or plateau, also decreases (Maqbool *et al.*, 2009). Figure 2.8 shows the equilibrium solubility at different heptane concentration.

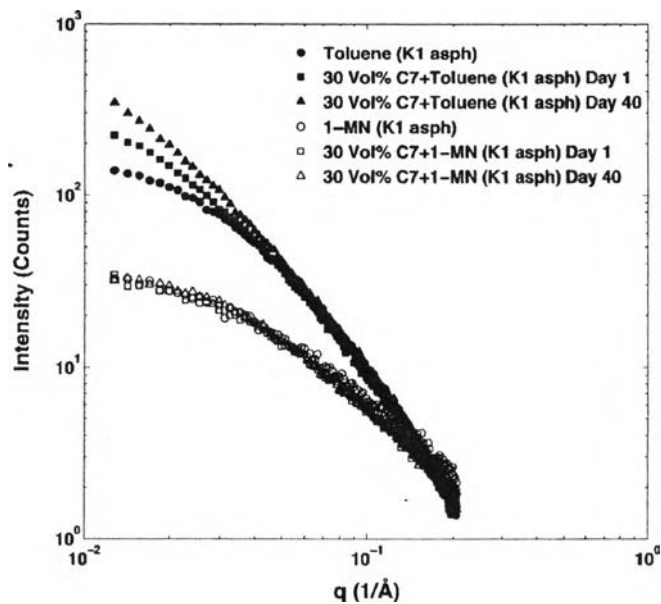




**Figure 2.8** Equilibrium solubility of asphaltenes in crude oil as a function of heptane concentrations for K-1 crude oil (Maqbool *et al.*, 2009).

## 2.5 Study of Asphaltenes by Small-angle Scattering Technique

Small-angle scattering is an analytical technique that makes use of the electron density difference to identify and measure the particle size, shape and polydispersity on the colloidal scale. In this research, the technique used is the small-angle X-ray scattering or SAXS. Asphaltene aggregates and their surroundings, either solvents or petroleum liquids, may differ in their electron density. If the electron density contrast is high enough, it is possible to detect the asphaltene aggregates in crude oils (Sheu *et al.*, 2006). The SAXS results is a plot of scattering intensity ( $I$ ) as a function of scattering vector ( $q$ ) as shown in Figure 2.9.



**Figure 2.9** The scattering profile of different asphaltenes sample (Haji-Akbari *et al.*, 2013).

The scattering intensity,  $I(q)$ , as a function of the scattering vector,  $q$ , can be used to estimate the size and shape of the scattering particle in the sample. The general expression for the scattering of a two-level system (e.g., particles in a liquid environment) is

$$I(q) = \phi(1 - \phi)\Delta\rho^2V_pP(q)S(q) \quad (2.1)$$

or in normalized form to isolate the scattering from the fractal clusters (Hoepfner *et al.*, 2013)

$$\frac{I(q)}{[\phi(1-\phi)\Delta\rho^2]} = V_pP(q)S(q) \quad (2.2)$$

Where  $I(q)$  is the scattering intensity

$q$  is the scattering vector which is  $\frac{4\pi \sin(\theta)}{\lambda}$

$\phi$  is the volume fraction of scattering particles (i.e. asphaltenes)

$\Delta\rho^2$  is the scattering contrast

$V_p$  is the particle volume

$P(q)$  is the form factor describing the particle shape

$S(q)$  is the structure factor describing the positional correlation

The size of asphaltene fractal clusters can be determined using the Zimm approximation which has been previously used to assess the radius of gyration of asphaltene fractal clusters (Roux *et al.*, 2001)

$$I(q) = I_0 \left[ 1 + \frac{(qR_g)^2}{3} \right]^{-1} \quad (2.3)$$

Where  $I_0$  is the zero-angle scattering intensity

$R_g$  is the radius of gyration

The fractal dimension ( $D_f$ ) can be extracted from small-angle scattering results by the following relation (Martin *et al.*, 1985)

$$I(q) = q^{-D_f} \quad (2.4)$$

If a sample has significant size polydispersity, the fractal dimension estimated by equation (5) will be lower than the true fractal dimension (Teixeira *et al.*, 1988). However, previous measurements have shown that the polydispersity in the asphaltene fractal cluster size is small enough so as to not influence the fractal dimension measurement (Fenistein *et al.*, 2001).

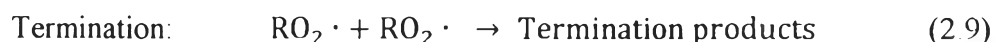
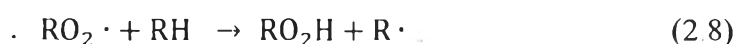
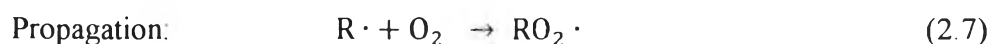
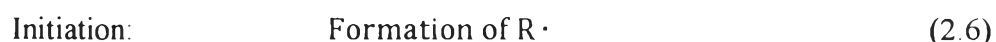
In a system of particles with different sizes and shapes, without particle-particle position correlation, the total scattering intensity is the summation of the scattering intensity from each individual asphaltene particle type (Sivia *et al.*, 2011).

$$I(q) = \sum I_i(q) \quad (2.5)$$

## 2.6 Role of Oxygen in Asphaltene Aggregation

Role of dissolved molecular oxygen on fuel is well known, as it drastically reduce the stability and increase the rate of deposit formation. Taylor (1974) investigated the parameters governing deposit formation from hydrocarbon jet fuels, including the dissolved oxygen. His results shown that removal of dissolved molecular oxygen content in the fuel significantly lower the formation of deposit. Furthermore, certain oxygen compounds, especially peroxide, also promote the deposit formation in deoxygenated hydrocarbon (Taylor, 1978).

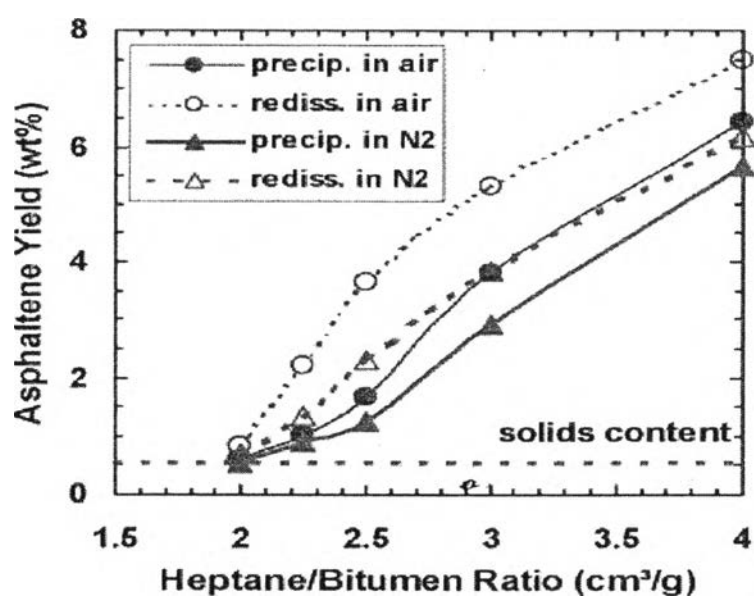
It is proposed that the oxygen is involved in the series of free radical chain reactions which leads to high mass polymerized hydrocarbons. Heneghan *et al.* (1994) and Erwin *et al.* (1997) investigated the oxidation of jet fuels and summarized the reaction mechanisms, which is autoxidation reaction, as shown in equation 2.6-2.12.



Where

- RH is hydrocarbon compound
- R · is a hydrocarbon alkyl radical species
- O<sub>2</sub> is the dissolved molecular oxygen
- RO<sub>2</sub> · is a peroxide radical
- RO<sub>2</sub>H is a hydroperoxide
- A · is an antioxidant radical
- AO<sub>2</sub> · is an antioxidant peroxide radical
- PH is proposed to be phenol (Heneghan *et al.*, 1994)

Since the oxygen can polymerized with hydrocarbons, it is reasonable to expect them to polymerized with asphaltenes and be the cause of asphaltene aggregation and deposition. Montanari *et al.* (1998) studied the interaction between asphaltenes radicals and dissolved molecular oxygen using Electron Paramagnetic Resonance (EPR) and found a weak spatial complex between aromatic moieties and oxygen molecules. Beck *et al.* (2005) investigated precipitation and redissolution of asphaltenes from mixtures of bitumen and n-heptane in air and nitrogen atmosphere. They observed an increase in the amount of asphaltenes precipitated after aeration at moderate temperature and suggested that it is because of the presence of oxygen as shown in Figure 2.10.



**Figure 2.10** Yield of asphaltenes precipitation and dissolution for Athabasca bitumen and n-heptane solution at 23°C in air and nitrogen atmosphere (Beck *et al.*, 2005).

Understanding the role of oxygen is crucial because most of researches are conducted under air atmosphere, which could lead to overprediction of asphaltene precipitation. Quantitative analysis of oxygen effects could be assessed by comparing the asphaltene precipitation under air and nitrogen environment.