CHAPTER II
LITERATURE REVIEW

2.1 Crude oil

Crude oil is a complex mixture of hydrocarbons and organic compounds that can contain sulfur, nitrogen, and oxygen and other metallic elements including nickel, vanadium, and iron (Hammami, *et al.*, 2007). In order to classify the components of crude oils, the oil production industry typically uses the SARA separation technique to separate crude oil fractions based on their differences in solubility. The four major fractions are saturates, aromatics, resins, and asphaltenes as shown in Figure 2.1.
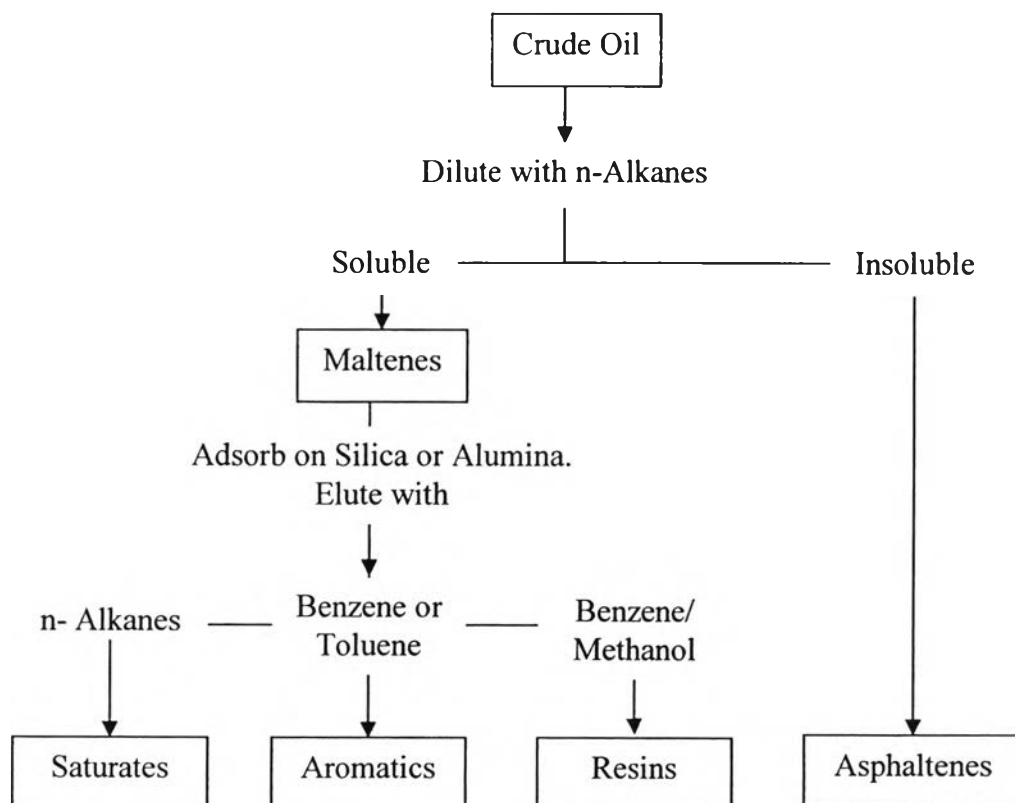

Figure 2.1 Schematic diagram of SARA separation (Wattana, 2004).

Based on the SARA separation technique, asphaltenes are the components that precipitate out of the crude oil by dilution with n-alkanes. The solution that remains is called maltenes also referred as deasphalted oil. Maltenes are then separated by adsorption on silica or alumina adsorbents and eluted with appropriate solvents like n–alkanes, benzene or toluene, and benzene/methanol to recover saturates, aromatics, and resins fractions, respectively.

Saturates consist of n-alkanes, branched alkanes, and cycloalkanes, all of which are nonpolar. Aromatics are hydrocarbons containing one or more ring structures. Resins are components of the crude oil that are thought to stabilize dispersions of asphaltenes in crude oil because of the ability of their polar heads to surround the asphaltene particles and their aliphatic tails to extend into the crude oil. In contrast to asphaltenes, resins are assumed to be soluble in crude oil. (Hammami, *et al.*, 2007). Asphaltenes are the heaviest and most polar fraction of the crude oil.

2.2   Asphaltenes

Asphaltenes are a class of molecules operationally defined (ASTM D 6560-00) as the fraction of crude oil that is insoluble in n-alkanes like n-heptane (referred to as a precipitant) and soluble in aromatics like toluene or benzene (referred to as a solvent) (ASTM International, 2005). Asphaltene precipitates are dark brown to black friable solids with no definite melting point (Wattana, 2004). They are classified based on the type of precipitant used, hence if heptane is used as the precipitant, they are called heptane asphaltenes, and if pentane is used, they are called as pentane asphaltenes. Speight (2007) demonstrated the effect of using different types of precipitants in the volume ratio of 40:1 (precipitant : crude oil) on the amount of asphaltenes that can precipitate out of the crude oil as shown in Figure 2.2. As the number of carbon atoms in the precipitant decreases, the yield of precipitated asphaltenes increases. This observation suggests that different n-alkanes have differences in their ability to separate asphaltenes from the crude oil.

The volume ratio of precipitant to oil affects the amount of asphaltenes that precipitates from the crude oil as shown in Figure 2.3 (Speight, 2007). At higher concentrations of precipitant, the yield of asphaltene precipitates plateaus to the total

amount of asphaltenes in the crude oil that can be precipitated by the particular precipitant.

Asphaltene stability in crude oils is a function of composition, temperature and pressure. Aside from the addition of n-alkanes, composition of crude oils can be changed by blending heavy viscous crude oils with light napthas (Gharfeh *et al.*, 2004), injecting gases into reservoir oils (Yang *et al.*, 1999), or adding stabilizing resins (Carnahan, *et al.*, 2007). Temperature and pressure changes can also cause precipitation of asphaltenes (Sheu, *et al.*, 2001; Espinat *et al.*, 2003; Kraiwattanawong *et al.*, 2007).
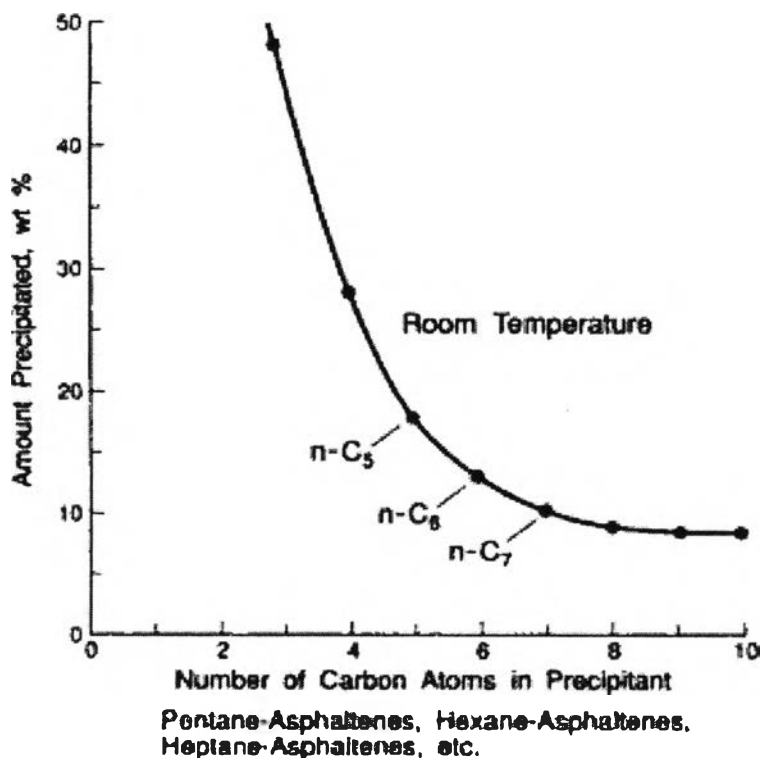

Figure 2.2 Yield of precipitated asphaltenes as a function of the carbon number of the n-alkane precipitant used (Speight, 2007).

Destabilized asphaltenes tend to aggregate together, to grow in size and to form a layer of precipitated solids on a surface that may lead to deposition of

asphaltenes. Precipitation is a necessary precursor to deposition but does not ensure deposition (Hammami, *et al.*, 2007).
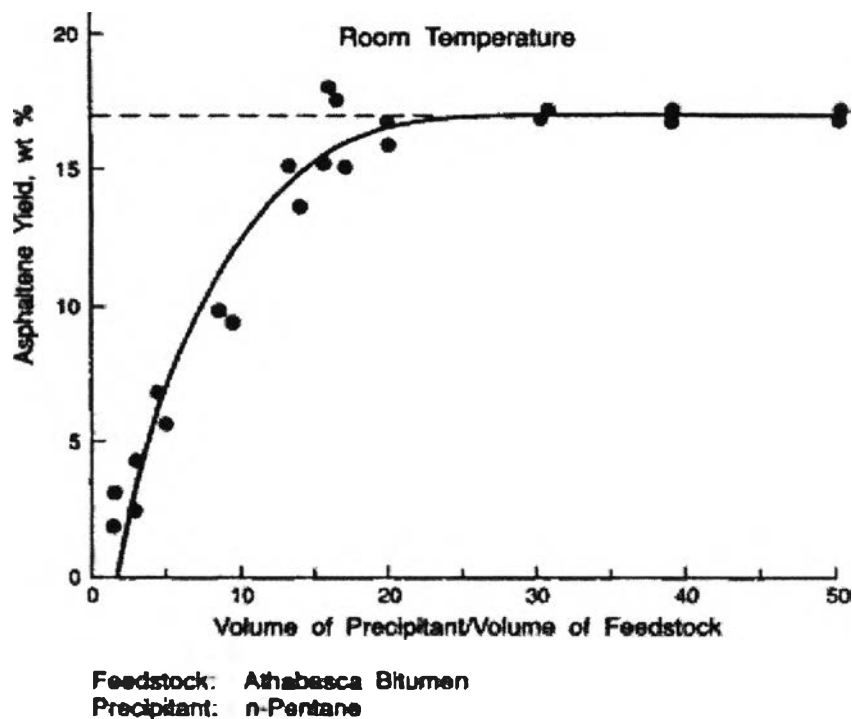

Figure 2.3 Yield of precipitated asphaltenes as a function of volume ratio of precipitant over oil feedstock (Speight, 2007).

Deposition of asphaltenes on oil well reservoirs, tubings, pipelines and production systems result in serious oil production problems that can lead to heavy economic losses (Pina, 2006). Deposition is the main problem of the industry, but precipitation studies are important in order to understand how to prevent deposition from occurring.

2.3 Asphaltene Precipitation

A majority of asphaltene precipitation studies use a thermodynamic approach focusing mainly on changes in composition, temperature or pressure. The common way to change the composition of crude oils is by adding n-alkanes, which act as

precipitants for asphaltenes. When a sufficient amount of precipitant is added to the crude oil, asphaltenes will precipitate out from the crude oil. The minimum amount of precipitant that causes asphaltenes to precipitate has been defined as the onset of precipitation (Pina, *et al.*, 2006). It is determined by using various techniques that measures the change in the bulk properties of the sample such as viscometry (Escobedo *et al.*, 1995), refractive index measurements (Wattana, 2003), and light absorbance measurements (Kraiwattanawong *et al.*, 2007), or by detecting precipitated asphaltene particles by optical microscopy (Wang *et al.*, 2001). A common issue with these techniques is that these measurements were conducted on short time scales. Wattana, *et al.* (2003) and Kraiwattanawong *et al.* (2007) made their measurements instantaneously after preparation of their samples. Escobedo *et al.* (1995) waited a few minutes to attain thermal equilibrium upon mixing crude oil and precipitant. Wang *et al.* (2001), however, waited for 24 hours to age their mixtures and took samples for optical microscopy. For all these studies, if there was no apparent observations of asphaltene precipitation during these conventional waiting times, the mixture was concluded to be stable, suggesting that it would never precipitate at any time. Additionally, Garcia & Correra (2007) have defined the minimum amount of precipitant to cause precipitation as the critical precipitant concentration for the oil. Below this critical precipitant concentration, they have concluded that the crude oil will remain stable and precipitation would not occur.

Recently, Angle *et al.* (2006) used optical microscopy to examine the onset of precipitation on a longer time scale. They demonstrated that the growth of asphaltene precipitates can be a slow process depending on the amount of heptane added. As shown in Figure 2.4, the precipitation of asphaltenes was delayed by 2.4 hours. This observation indicates the onset of asphaltene precipitation is not only dependent on the precipitant concentration but also on time. However, they have used a model system where heptane is added into the crude oil, which was diluted with toluene.

Rastegari *et al.* (2004) also studied the flocculation kinetics of precipitated asphaltenes. They used a model system of precipitated asphaltenes, which are dissolved in toluene and then, added heptane as a precipitant. After addition of sufficient amount of heptane, asphaltenes precipitated with a size of $1\mu m$ and its

growth over time was monitored using a particle analyzer. They have observed that precipitated asphaltenes flocculate over time and form loose fractal-like flocs.

Results from a model system using toluene as a diluent cannot represent the actual precipitation behavior of asphaltenes in crude oils. A real system would only involve using n-alkanes to precipitate the asphaltenes. Since toluene acts as a good solvent and hinders asphaltene precipitation, the delay in precipitation observed by Angle, *et al.* (2006) could be attributed due to the addition of toluene. The model system used by Rastageri, *et al.* (2004) cannot represent asphaltene precipitation in crude oils. Kinetic effects on toluene-diluted crude oil systems would be different from the precipitation kinetics in pure crude oils.
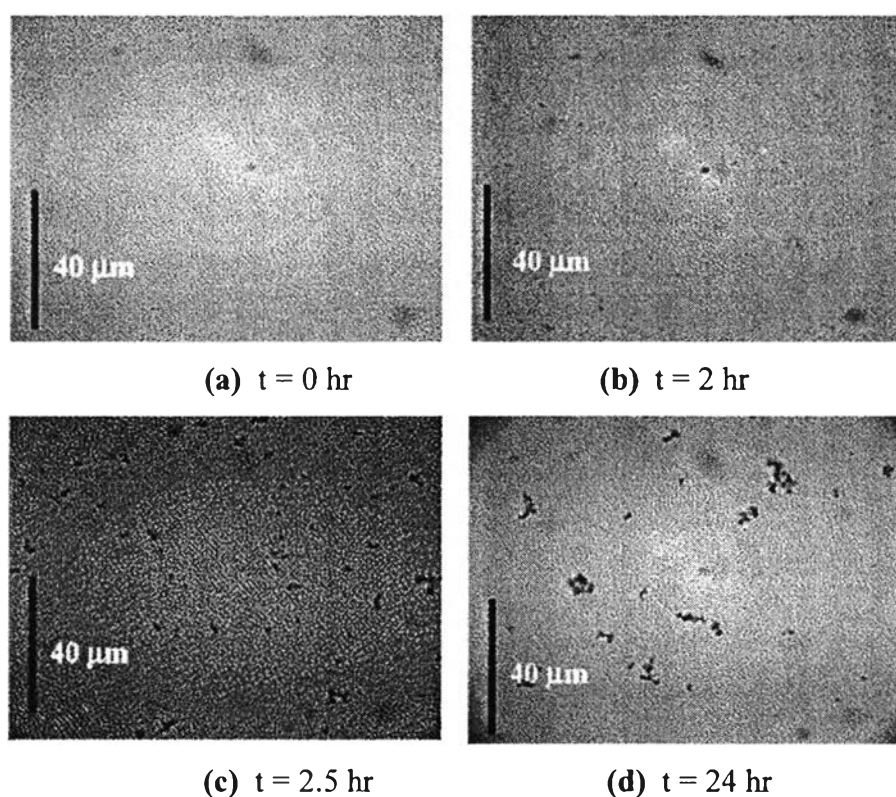

(a) t = 0 hr   (b) t = 2 hr

(c) t = 2.5 hr   (d) t = 24 hr

Figure 2.4 Micrographs of asphaltene particles precipitated at different times after addition of heptane on crude oil diluted with toluene (Angle *et al.*, 2006).

In this regard, Maqbool *et al.* (2008a) studied a heavy Alaskan crude oil (K1 oil) and precipitated the asphaltenes by using heptane. Unlike other studies, toluene

was not used to dilute the crude oil. This system described actual kinetic behavior of asphaltene precipitation from crude oils. They have demonstrated that time has a significant effect on asphaltene precipitation. Their sample was prepared by adding gradually heptane into a well-stirred crude oil. Afterwards, frequent sampling of the mixture was done over time and each sample was analyzed under an optical microscope for the presence of asphaltene precipitates. It has been observed that asphaltene particles can slowly grow over time to a well-defined size of 0.5μm, depending on the heptane concentration. This 0.5μm criteria, which was used by Wang and Buckley (2003) is comparable to the typical pore size of reservoir rock which has practical implications in plugging cause by asphaltene precipitation. The time that has elapsed for asphaltene precipitates to reach 0.5μm is defined as the precipitation onset time. In Figure 2.5, the plot shows the precipitation onset time for samples with different heptane concentrations. Contrary to other research by Wang and Buckley (2003), Wattana, et al. 2003, Kraiwattanawong, et al. (2007) and Escobedo and Mansoori (1995), Maqbool et al. (2008a) have been able to demonstrate that asphaltene precipitation is not instantaneous but a function of both precipitant concentration and time.
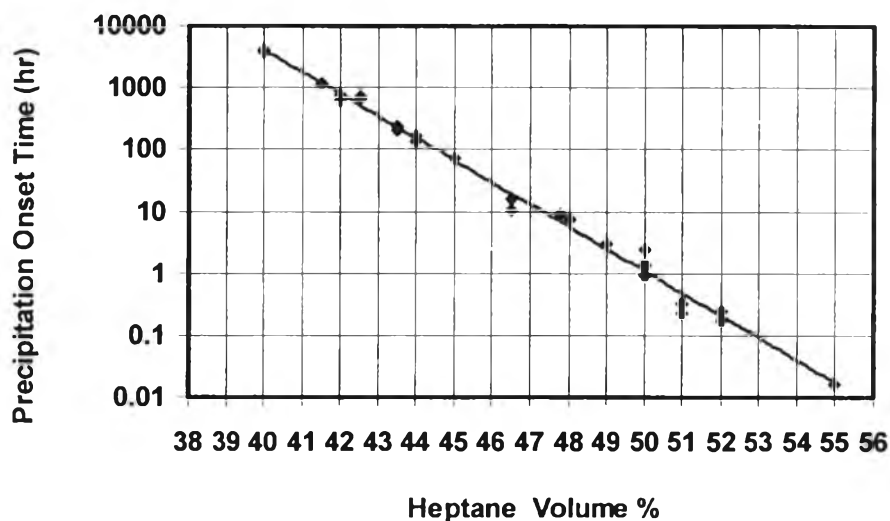

Figure 2.5 Precipitation onset time for K1 crude oil at different heptane volume %. (Maqbool, et al., 2008a)

Maqbool *et al.* (2008a) also used the techniques developed by Wattana, *et al.* (2003) and Kraiwattanawong, *et al.* (2007) to determine the onset of precipitation for K1 crude oil and compared those results with optical microscopy. The reported onset of precipitation for K1 oil was at a heptane volume fraction, $\varphi_{heptane}= 0.55$ for the refractive index measurement and $\varphi_{heptane} = 0.57$ for the light absorbance measurement. However as shown in Figure 2.5, asphaltenes has been observed to precipitate at heptane concentrations much below $\varphi_{heptane}= 0.55$.

Maqbool *et al.* (2008a) have also developed a novel centrifugation-based separation technique that quantified the amount of precipitated asphaltenes over time. Figure 2.6 shows the yield of precipitated asphaltenes as a function of time for a 46.5 vol% heptane in K1 oil.
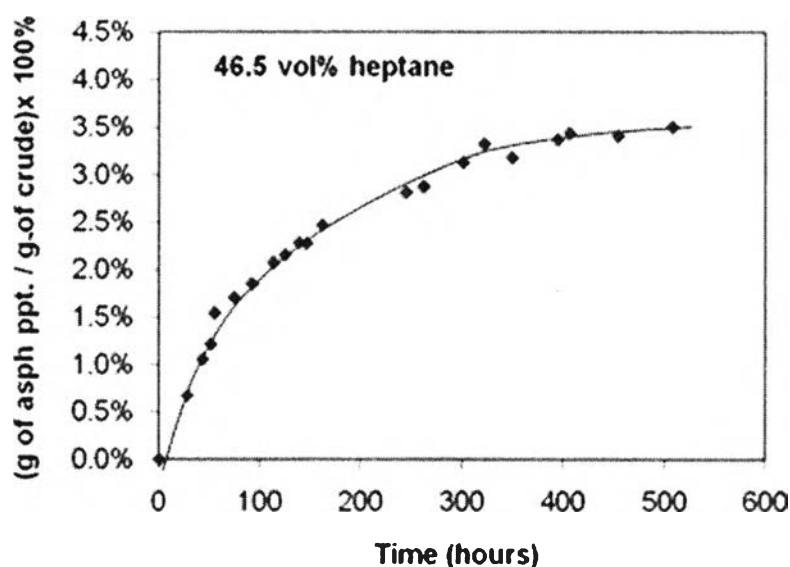

Figure 2.6 Yield of precipitated asphaltenes as a function of time using K1 crude oil at 46.5 vol% heptane. (Maqbool *et al.*, 2008a)

Figure 2.6 shows that the yield of precipitated asphaltenes gradually increases and reaches a plateau value after more than 500 hours. This plateau value corresponds to the equilibrium amount of asphaltenes that can be precipitated from a 46.5 vol% heptane in K1 crude oil. Maqbool, *et al.* (2008a) have also shown that as the heptane concentration increases, the equilibrium yield of precipitated asphaltenes

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 precipitated asphaltenes.

Maqbool, et al. (2008a) have only observed the kinetic effects of asphaltene precipitation on one particular crude oil, which might be an unique characteristic of the studied oil. In order to verify if the observed kinetic effects are universal for different crude oils, different crude oils from different oil fields, physical properties and chemical composition were tested in this study.

2.4   Effect of the type of n-alkanes on asphaltene precipitation kinetics

Aside from n-heptane, other pure n-alkanes can be used to precipitate asphaltenes. As mentioned by Speight (1999) in Figure 2.1, at a 40:1 volumetric ratio of precipitant : oil, the yield of the total asphaltenes that are precipitated increases as the carbon number of the n–alkane precipitant decreases. Speight (1999) has concluded that the type of n-alkane used to precipitate asphaltenes has a significant effect on the amount of asphaltenes that can be precipitated from the crude oil. On the other hand, Wang and Buckley (2001) studied the effect of different types of n-alkane precipitants at the onset of precipitation. They have demonstrated that the type of alkane has a significant effect on onset of precipitation, as shown in Figure 2.7. It appears that as the carbon number of the n-alkane increases, the required concentration to induce asphaltene precipitation generally increases from n-hexane and starts to decrease from n-octane or n-nonane to n-pentadecane, showing a volume maximum.

Wiehe, et al. (2005) also observed similar trends based on experimental results from different crude oils. Cimino et al. (1995) and Wiehe, et al. (2005) were able to model such phenomenon by applying the Flory-Huggins theory of mixing which accounted the differences in molecular sizes between the asphaltenes and the n-alkane precipitants that were used for precipitation. However, the Flory-Huggins theory has been originally developed for polymer chain molecules. The nature of asphaltenes being polyaromatic molecules rather than polymer chains may limit the
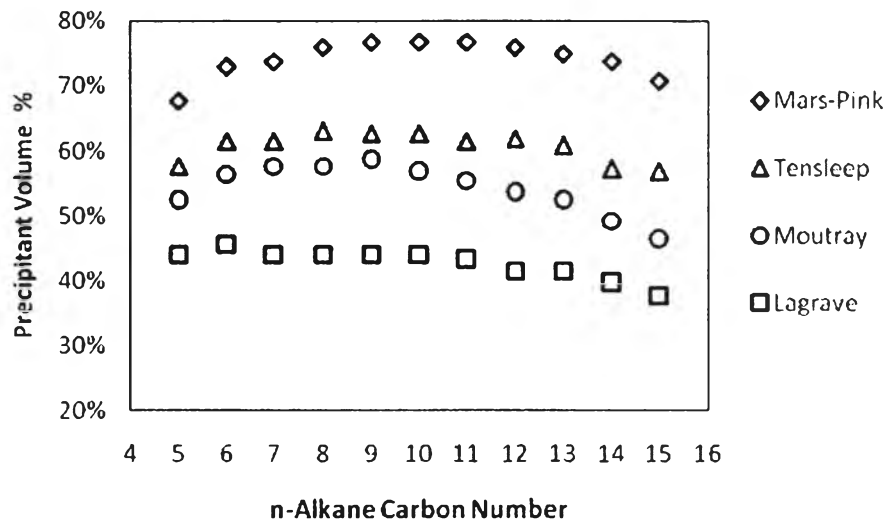
Figure 2.7 Precipitant volume % at the onset of precipitation for different n-alkanes using various crude oils. (Adapted from Wang *et al.,* 2001).

application of the Flory-Huggins theory for asphaltene precipitation. Moreover, the Flory-Huggins approach assumes that asphaltenes undergo a phase change from a dissolved state to a different phase. On the contrary, recent research have shown that asphaltenes in crude oil exist as nanoparticles with a size of ~ 2nm (Betancourt, *et al.*, 2009) and can further aggregate (Mason and Lin, 2003a, Mason and Lin, 2003b). These recent findings may suggest that the aggregation of asphaltene nanoparticles rather than the phase change of asphaltenes may be the right approach in understanding asphaltene precipitation.

Present studies have neglected the significant effects of time during asphaltene precipitation (Wang and Buckley (2001); Wiehe, *et al.* (2005); Cimino, *et al.* (1995)). To address this issue, this study had investigated the effect of the type of n-alkane on the kinetics of asphaltene precipitation.

2.5   Modeling of the Kinetics of Asphaltene Precipitation by a Geometric Population Balance Model

The precipitation of asphaltenes from crude oil has been established to be dependent on the concentration of the precipitant and time (Maqbool, *et al.*, 2008a).

Furthermore, Maqbool, Raha and Fogler (2008b) have developed a geometric population balance model that was able to describe the kinetics of asphaltene precipitation.

The geometric population balance model is based on the nanoaggregation of asphaltenes destabilized because of the addition of a precipitant. It assumed that after addition of the precipitant, asphaltenes are rapidly destabilized. Then, the destabilized asphaltenes tend to aggregate into bigger aggregates over time. The total amount of destabilized asphaltenes by a particular precipitant concentration is estimated from the equilibrium amount of precipitated asphaltenes from centrifugation experiments.

The geometric population balance model is based on the classical Smoluchowksi equation which describes the evolution of aggregates based on the aggregation of particles of various sizes (Elimelech, *et al.*, 1995). Initially, aggregation starts with the collision of identical particles (same sizes) referred as the primary units. These primary units are the asphaltenes that were rapidly destabilized after addition of the precipitant. Then, aggregation proceeds with the collision of particles of different sizes. The model used a geometric sectioning approach to account the number of primary units in an aggregate. For example, the k-th aggregate is described as having R^{k-1} number of primary units where R is the geometric spacing used. By doing a geometric sectioning approach, the number of simultaneous ordinary differential equations (ODEs) that are required to be solved is significantly minimized (Maqbool, *et al*, 2008b).

Rastageri , *et al.* (2004) developed an asphaltene flocculation kinetics model which is based on the discretization of the volume of aggregating asphaltenes. However, this assumption is invalid because as aggregates grow bigger, they tend to become less compact and volume is not conserved. On the other hand, the geometric population balance developed by Maqbool, Raha and Fogler (2008b) is based on the conservation of the number of primary asphaltene units that was initially destabilized by the precipitant. As asphaltenes aggregate, the number of primary units is always conserved.

The geometric population balance model describes the evolution of aggregates as its primary particles grow to bigger aggregates. The net rate of generation of the i-th aggregate is given by (Maqbool $et\ al.$, 2008b)

$$\frac{dC_i}{dt} = \left[\frac{K_{i-1,i-1}}{R}C_{i-1}^2\right] + \left[C_{i-1}\sum_{j=1}^{i-2}K_{i-1,j}\frac{R^{j-1}}{R^{i-1}-R^{i-2}}C_j\right] - \left[C_i\sum_{j=1}^{i-1}K_{i,j}\frac{R^{j-1}}{R^i-R^{i-1}}C_j\right] - \left[C_i\sum_{j=i}^{N-1}K_{i,j}C_j\right]$$

(2.1)

where C_i represents the molar concentration of i-th aggregate (kmol m^{-3}), $K_{i,j}$ represents the collision kernel describing the collision of the i-th and j-th aggregate and R represents the geometric spacing between two subsequent aggregates.

The first term in Equation (2.1) accounts for the generation of the i-th aggregates from collision of i-1 aggregates. The second term accounts for the generation of i-th aggregate from collision of i-1 aggregates with smaller j-th aggregates ($j < i$ -1). The third term accounts of the depletion of i-th aggregates due to its collision with a smaller j-th aggregate ($j < i$), forming bigger i+1 aggregates. The fourth term accounts for the depletion of the i-th aggregates due to their collision with j-th aggregates that are equal to or larger than the i-th aggregates ($j \geq i$), forming bigger j+1-th aggregates. The total number of primary units across all species at any instant should be equal to the total primary units that are initially present.

In Equation (2.1), K_{ij} represents the collision kernel, which accounts for the kinetic effects of the model. K_{ij} is a product of the collision frequency, α_{ij} between species i and j, and the collision efficiency, β. Not every collision of i and j particles result to a successful aggregation, such that the collision efficiency has been taken into account in the model. The collision kernel used in this model is the Brownian flocculation kernel which accounts for the aggregation of destabilized primary asphaltene particles starting from nanoaggregate size. It is noted that the viscosity of the medium could significantly affect the collision kernel. The Brownian flocculation kernel, $K_{i,j}$ which describes the diffusion limited aggregation, is expressed as

$$K_{i,j} = \frac{2RT(d_i+d_j)^2}{3\mu_m(d_id_j)}\beta$$

(2.2)

where d_i and d_j = diameter of the colliding aggregates i and j (m)

μ_m = viscosity of the medium (kg m^{-1} s^{-1})

R = universal gas constant (J kmol^{-1} K^{-1})

T = absolute temperature (K)

The only unknown parameter in Equation (2.2) is the collision efficiency, β which is estimated from the experimental results.

In order to validate the geometric population balance model, the simulation results were compared to the experimental results that are based on the yield of precipitated asphaltenes that were separated using the centrifugation-based separation technique. Equation (2.1) was solved using the Brownian collision kernel and the initial conditions to estimate the concentration of aggregates of different number of primary particles as a function of time. The aggregate domain is discretized to 40 geometric sections, using the geometric scaling $R = 2$, which is sufficient to describe aggregation of asphaltenes from its primary units to the largest possible asphaltene aggregate with a diameter of 14μm and 2^{39} number of primary particles. The diameter of the spherical asphaltene primary unit is estimated from its molecular weight and density. The estimated diameter of the asphaltene primary particle used in the model is ~1.5 nm, which is similar to the size of asphaltene nanoaggregates as determined by Betancourt, *et al.* (2009). The 40 geometric sections generates 40 nonlinear ODEs that are solved simultaneously using Runge-Kutta, Bogacki and Sampine method (Matlab routine ODE23). The concentration of each i-th aggregate as a function of time, $C_i(t)$ was then calculated. The evolution of separated aggregates by centrifugation, $S_A(t)$ is estimated to be

$$S_A(t) = \frac{\sum_{i=1}^{N} R^{i-1} M_{w,A} s_i C_i(t)}{w_o} \qquad (2.3)$$

where $S_A(t)$ is the mass of separated asphaltene per unit mass of oil
         (kg asphaltene/kg oil),

w_o is the mass of oil per unit volume of mixure (kg m^{-3}),

s_i is the separation efficiency of i-th aggregate in the centrifuge.

$S_A(t)$ represents the accumulated yield of asphaltenes from the i-th aggregate to the N-th aggregate at time, t. $S_A(t)$ can be compared with the yield of precipitated asphaltenes from centrifugation experiments.