



CHAPTER IV RESULTS AND DISCUSSION

4.1 Detection of the onset of asphaltene precipitation

Optical microscopy was used to observe the evolution of asphaltene precipitates from the crude oil. After gradually mixing heptane with GM2 oil, samples were taken at different times and analyzed under the optical microscope for the presence of asphaltene precipitates.

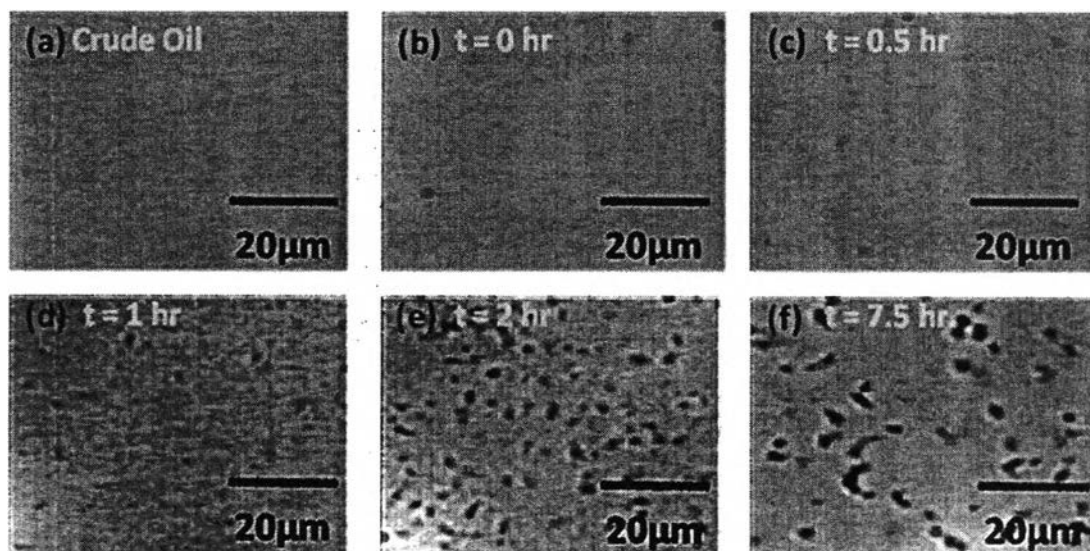


Figure 4.1 Micrographs of 35 vol% heptane in GM2 oil at different times. (a) Pure crude oil as base case. (b) At $t = 0$ after addition of heptane. (c) At $t = 0.5$ hour. (d) At $t = 1$ hour. (e) At $t = 2$ hour. (f) At $t = 7.5$ hour.

Figure 4.1 shows the micrographs of a 35 volume % heptane in GM2 oil taken at various times. Centrifuged GM2 oil was used for the study and shows a neat base case image as seen in Figure 4.1(a). The image remains neat from time $t = 0$ after heptane addition up to $t = 0.5$ hour, as shown in Figure 4.1(b) and 4.1(c), respectively. However, after $t = 1$ hour (Figure 4.1 (d)), few hazy asphaltene particles of about $0.2 \sim 0.3 \mu\text{m}$ in diameter precipitate out from the crude oil mixture. The

time $t = 1$ hour is referred to as the haze onset time. After $t = 2$ hours, asphaltene precipitates have grown to about $0.5 \sim 0.6 \mu\text{m}$ in diameter as shown in Figure 4.1(e) and appear to have distinct edges that can be sharply focused by the microscope. The time $t = 2$ hours is defined as the precipitation onset time when asphaltene precipitates have grown to $0.5 \sim 0.6 \mu\text{m}$ in diameter. As time progresses, asphaltene precipitates continue to grow and aggregate as shown in Figure 4.1(f) to a size of about $1 \sim 2 \mu\text{m}$ after 7.5 hours.

For a 43 vol% heptane in GM2 oil, hazy asphaltene particles can be seen right after preparation of the sample as shown in Figure 4.2(a). Asphaltene precipitates of $0.5 \sim 0.6 \mu\text{m}$ in size were observed after 5 minutes (Figure 4.2(b)). Precipitated asphaltenes continue to aggregate and grow in size over time as shown in Figures 4.2 (c) – (f). The 43 vol% heptane concentration represents the instantaneous onset of precipitation for GM2 oil, which is the minimum amount of heptane required to instantaneously precipitate asphaltenes. Also, at heptane concentrations higher than 43 vol%, precipitation of asphaltenes is instantaneous and precipitated asphaltenes would aggregate and form bigger flocs.

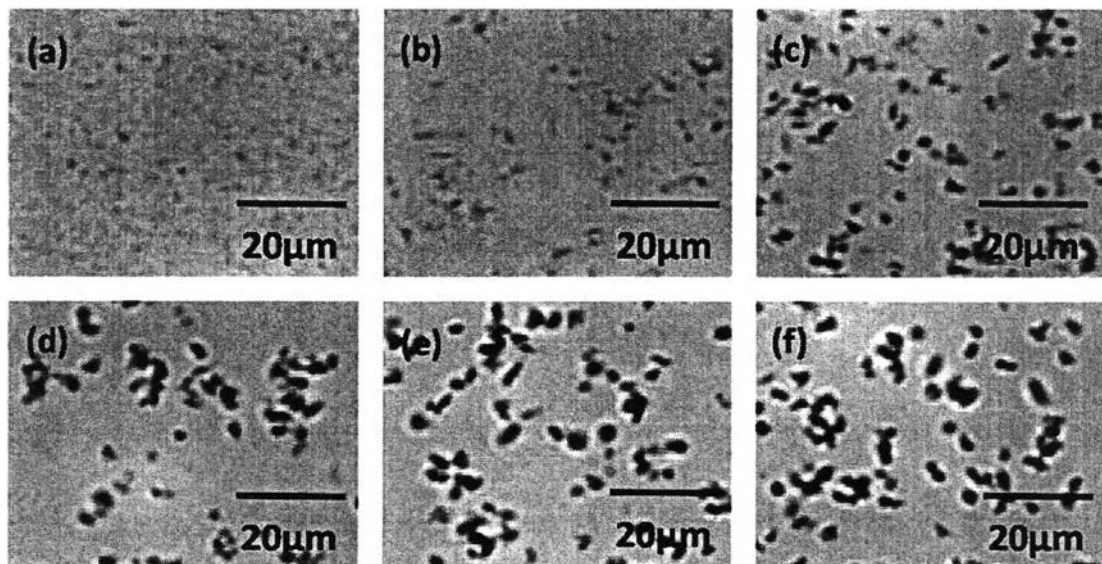


Figure 4.2 Growth of asphaltene precipitates for 43 vol% heptane in GM2 oil. (a) At $t = 0$ min. (b) At $t = 5$ min. (c) At $t = 1$ hour. (d) At $t = 2$ hour. (e) At $t = 10$ hours. (f) At $t = 24$ hours.

These experimental results show that asphaltenes precipitate out of the crude oil even below the critical precipitant concentration which contradicts the previous research which was done only for short time scales. Figure 4.3 shows the detection time for the onset of haze and onset of precipitation of asphaltenes from GM2 crude oil at different heptane volume %. It shows that beyond the conventional waiting time of up to 24 hours, asphaltenes continue to precipitate. As shown in Figure 4.3, a 27 vol% heptane mixture has a precipitation onset time of 40 hours. If we limit our experiments to the conventional waiting time of 24 hours as done by Wang *et al.* (2001) and use the concept of the critical precipitant concentration, we would be misled to conclude that this system is stable and would not precipitate asphaltenes. However, this conclusion is not true. After 40 hours, this 27 vol% heptane – GM2 crude oil mixture becomes unstable and asphaltenes precipitate out.

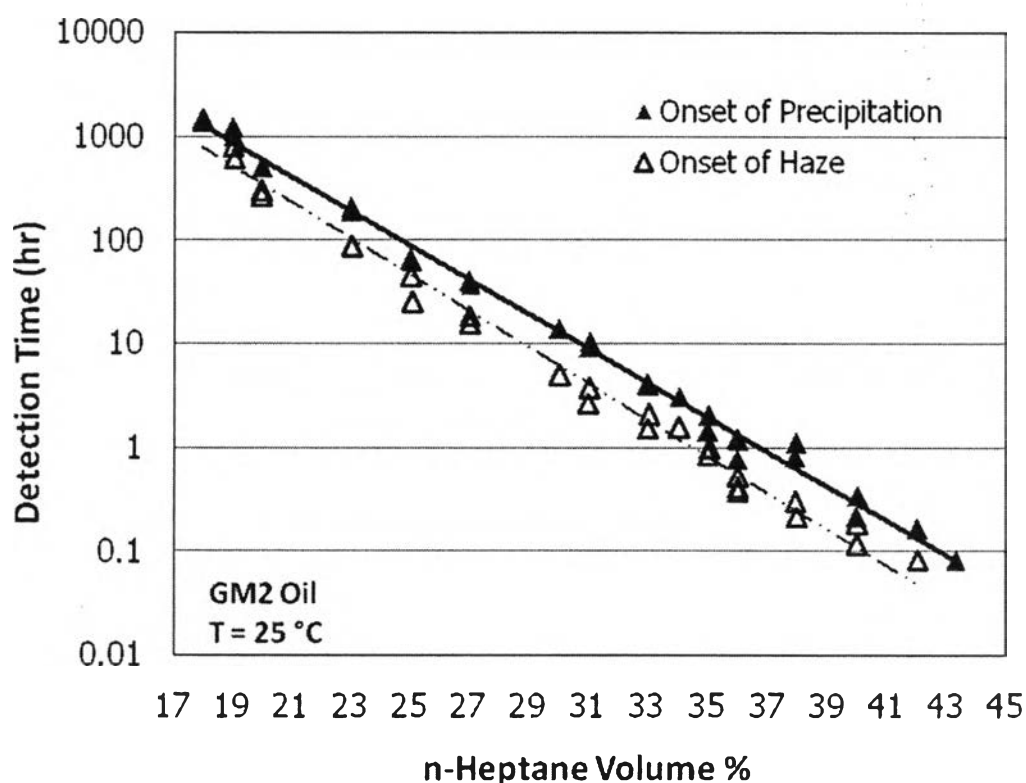


Figure 4.3 Detection time for the onset of haze and onset of precipitation for GM2 crude oil at different heptane volume %.

Figure 4.3 shows the detection time is exponentially related to the heptane concentration. Asphaltenes can precipitate from crude oils ranging from few minutes to months, depending on the precipitant concentration. This observation clearly invalidates the concept of a critical precipitant concentration for a specific crude oil and concludes that asphaltene precipitation is a function of both the precipitant concentration and time.

4.2 Universality of the kinetics of asphaltene precipitation

It could be argued that the observed kinetic effects could be specific to the particular crude oil that was tested. Thus, different crude oils (GM2 oil, N2 oil, K1 oil) were tested to examine their kinetic effects. N2 and K1 oils come from different oils fields in the Alaskan North Slope while GM2 oil comes from an oil field in the Gulf of Mexico. Table 4.1 shows the comparison of the SARA analysis, physical properties and the minimum volume % of heptane for instantaneous precipitation for the three different oils used in this study.

Table 4.1 SARA analysis, physical properties and minimum heptane volume% (for precipitation within 5 minutes) for different crude oils.

| SARA Fraction | K1 Oil | GM2 Oil | N2 Oil |
|---|--------|---------|--------|
| Saturates (wt %) | 41.0 | 46.2 | 55.1 |
| Aromatics (wt %) | 28.5 | 41.8 | 23.6 |
| Resins (wt %) | 18.4 | 8.4 | 17.3 |
| n-C7 Asphaltenes (wt %) | 10.9 | 3.6 | 2.4 |
| Density (g/mL at 25°C) | 0.9218 | 0.8619 | 0.8737 |
| Viscosity (cP at 25°C) | 160 | 15.7 | 13.9 |
| Minimum n-C7 vol% (within 5 minutes waiting time) | 55 | 43 | 60 |

Figure 4.4 shows the precipitation onset time at different heptane volume % for 3 different crude oils. These results confirm that kinetic effects on asphaltene precipitation are universal for different oils.

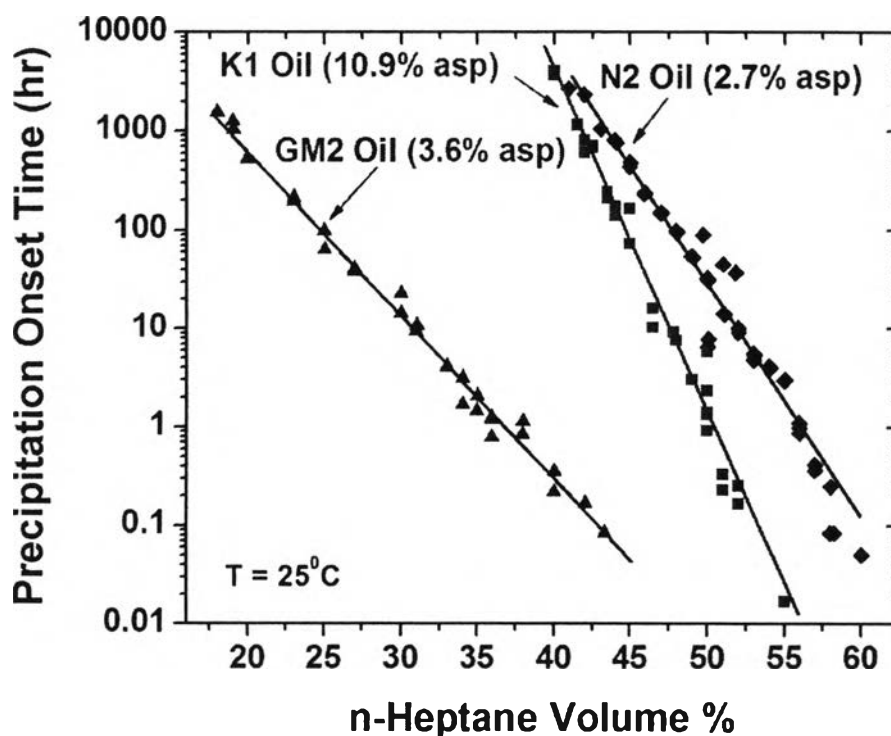


Figure 4.4 Precipitation onset time at different heptane volume % for GM2, K1 and N2 oils. (K1 oil experiments done by Maqbool, 2008a).

However, the three different oils precipitate within 5 minutes at different heptane volume %. Asphaltenes instantaneously precipitate from GM2 oil at 43 heptane vol% as compared to K1 oil at 55 heptane vol% and N2 oil at 60 heptane vol%. For a given precipitation onset time, GM2 oil precipitates asphaltenes with the least heptane volume%, followed by K1 oil and N2 oil. It appears that GM2 is the least stable among the 3 oils since asphaltenes from GM2 oil start to precipitate at lowest heptane concentration.

The asphaltene content of the three oils varies from increasing order of increasing order as N2 oil (2.7 wt%), GM2 oil (3.6 wt%), and then K1 oil (10.9 wt%). N2 oil has the least amount of asphaltenes and appears to be the most stable

oil among the three oils. However, the stability of K1 oil is in between GM2 oil and N2 oil even though it has the highest asphaltene content. This observation indicates that the stability of the crude oil is independent of its asphaltene content. This conclusion is also in agreement with the findings of Wattana (2004) where she showed that the asphaltene content of the oil is not related to the minimum amount of precipitant required for precipitation.

The SARA analysis of crude oils may be able to give an indication towards the stability of the crude oil against asphaltene precipitation. Consider the asphaltenes that are stable in the neat crude oil, they are destabilized after addition of n-alkane precipitants. Saturates and aromatics in the crude oil could resemble the components that respectively precipitate and dissolve the asphaltenes in the crude oil. A balance of saturates and aromatics could provide stability to the asphaltenes in a particular oil. Comparing the saturates/aromatics ratio of different oils may offer an insight to the stability of the asphaltenes in the crude oil.

Table 4.2 shows that an increasing ratio of saturates/aromatics components of the oil leads to an increase in minimum heptane volume % needed to induce asphaltene precipitation for a 5-minute waiting period. Additionally, the 3 different oils come from different sources and have different physical properties and chemical composition. The asphaltenes from these oils may have different physical and chemical properties and could behave differently in the crude oil. Although the N2 oil has the highest saturates/aromatics ratio of the 3 oils, it requires the highest amount added heptane to destabilize its asphaltenes. However, GM2 oil, having the lowest saturates/aromatics ratio suggests that its asphaltenes are least stable and would precipitate with the least amount of heptane. These results may suggest that

Table 4.2 Comparison of the saturates/aromatics ratio of crude oils

| Parameter | GM2 Oil | K1 Oil | N2 Oil |
|--|----------------|---------------|---------------|
| Saturates/Aromatics | 1.1961 | 1.4386 | 2.3347 |
| Minimum n-C7 vol% (5 minute waiting time) | 43 | 55 | 60 |

the N2 asphaltenes are more tolerant towards destabilization by heptane addition as compared to other asphaltenes from the 2 oils. These results show that the saturates/aromatics ratio could provide an indication to the stability of asphaltenes from different crude oils. However, this hypothesis needs to be proven by characterizing the asphaltenes precipitated from different crude oils in terms of its metal content, polarity, or aromaticity. A compositional analysis of the crude oil could give indications which abundant fraction can affect asphaltene stability.

4.3 Quantification of the amount of asphaltenes precipitated over time

Microscopic observations have shown that asphaltenes precipitate out of the crude oil solution both as a function of heptane concentration and time. In order to quantify the rate of precipitation of asphaltenes from crude oil – heptane mixtures, a centrifugation–based separation technique developed by Maqbool, *et al.* (2008a) is used. Based on Stokes law, particles with larger diameters dispersed in a liquid medium settle faster due to gravity (Allen, 1981; Geankoplis, 1993). Applying centrifugal force on these particles increases the rate of settling. The operating parameters for Eppendorf microcentrifuge were fixed at 10,000 rpm for 10 minutes. In order to ensure that the operating conditions are sufficient enough, the cutoff particle diameter was calculated and evaluated. The cutoff particle diameter, D_m is the minimum size of the particle suspended in the medium that can be totally separated. It is dependent on the geometry of the centrifuge, density and viscosity of liquid medium, density of the particle, and operating conditions of the centrifuge (*See Appendix G for derivation*).

$$D_m = \sqrt{\frac{18\mu \ln(R/S)}{(\rho_p - \rho_f)\omega^2 t}} \quad (4.1)$$

where R = distance from the axis of rotation to the bottom of the tube (m)

S = distance from the axis of rotation to the surface of the fluid (m)

L = distance from the surface of the fluid to the bottom of the tube (m)

μ = viscosity of the medium ($\text{kg m}^{-1} \text{s}^{-1}$)

ρ_p, ρ_f = density of the particle and fluid medium, respectively (kg m^{-3}).

ω = angular velocity (rad sec^{-1})

t = centrifugation time (sec)

The average cutoff diameter was calculated at 0.25 μm . Asphaltene precipitates are initially detected as haze particles at 0.2 – 0.3 μm . Thus, the operating conditions are efficient to centrifuge most of the asphaltenes larger than 0.25 μm .

Upon destabilization of asphaltenes, asphaltenes precipitate and aggregate over time forming bigger flocs. Asphaltene precipitates bigger than the cutoff particle diameter are totally separated while some smaller precipitates are also separated but with a lower separation efficiency. As time progresses, these smaller precipitates continue to grow and reach the cutoff diameter.

Figure 4.5 shows the yield of precipitated asphaltenes from a 31 vol% heptane in GM2 oil as a function of time. The y-axis is plotted as the mass of precipitated asphaltenes per mass of crude oil in the mixture while the x-axis is the time elapsed after preparation of the sample. A 31 vol% heptane mixture has a precipitation onset time of 10 hours. Figure 4.5 shows that as time increases, the amount of precipitated asphaltenes gradually increases until it reaches a constant plateau value of 0.90% at around 700 hours. This plateau value is the equilibrium amount of asphaltenes that can be precipitated when 31 vol% heptane is added to GM2 oil.

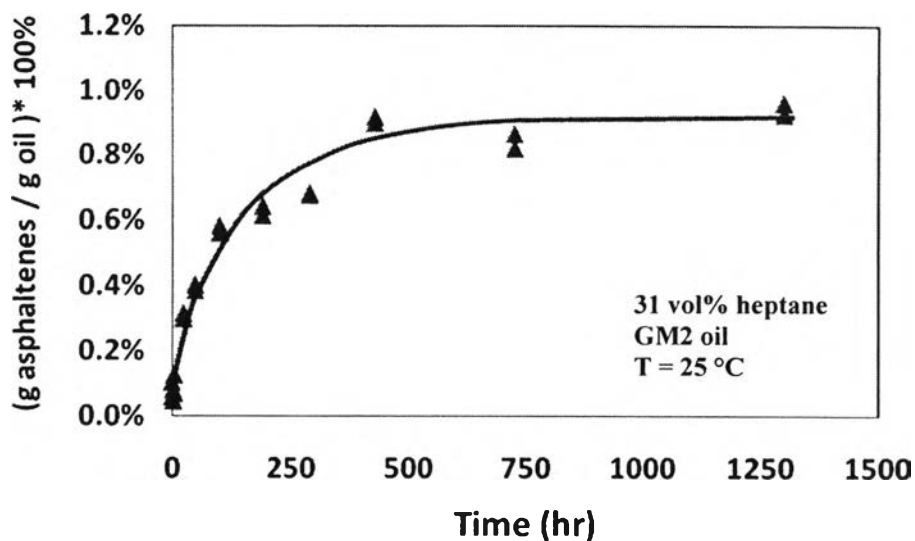


Figure 4.5 Yield of precipitated asphaltenes as a function of time for 31 vol% heptane in GM2 oil.

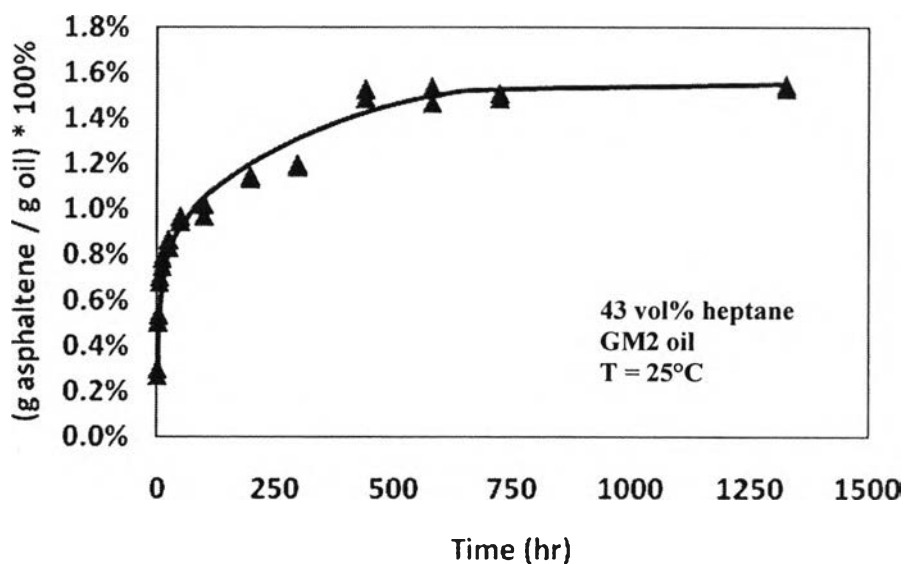


Figure 4.6 Yield of precipitated asphaltenes as a function of time for 43 vol% heptane in GM2 oil.

A 43 vol% heptane mixture precipitates asphaltenes within the precipitation onset time of 5 minutes. As can be seen in Figure 4.6, 5 minutes after the preparation of the sample, 0.28% of asphaltenes have already precipitated. As time progresses,

the amount of precipitated asphaltenes increases significantly. After 24 hours, the asphaltene yield is 0.85%. However, the equilibrium yield of 1.51% is only reached after 580 hours.

Figure 4.7 shows the yield of precipitated asphaltenes for various heptane vol% as a function of time. As the heptane vol% increases, the equilibrium yield of precipitated asphaltenes increases while the time required to reach the equilibrium plateau value decreases. The rate of precipitation increase as the heptane vol% increases. However, it should be noted that it takes days, weeks or months to reach the equilibrium yield of precipitated asphaltenes. In developing thermodynamic models, the equilibrium yield of precipitated asphaltenes should be used instead of values that were determined after short waiting scales. This work confirms the results from microscopy experiments that asphaltene precipitation is a function of time.

4.4 Solubility of asphaltenes in crude oil – heptane mixtures

In order to model the precipitation of asphaltenes, knowing the amount of soluble asphaltenes in the crude oil – heptane mixture is essential. A particular concentration of heptane in the crude oil can only precipitate a limited amount of asphaltenes while the remaining asphaltenes are kept soluble in the crude oil. To calculate the equilibrium amount of soluble asphaltenes in the crude oil– heptane mixture, the plateau values for each heptane concentration from Figure 4.7 are subtracted from the total amount of asphaltenes in the crude oil. At 95 vol% heptane, the total yield of precipitated asphaltenes (mass asphaltenes / mass crude oil) is at $2.82\% \pm 0.10\%$. There is a difference between the asphaltene content determined by SARA analysis (3.6%) and the total asphaltenes by centrifugation technique ($2.82\% \pm 0.10\%$). This deviation is due to the differences in the techniques used. (*See Appendix E for the explanation*).

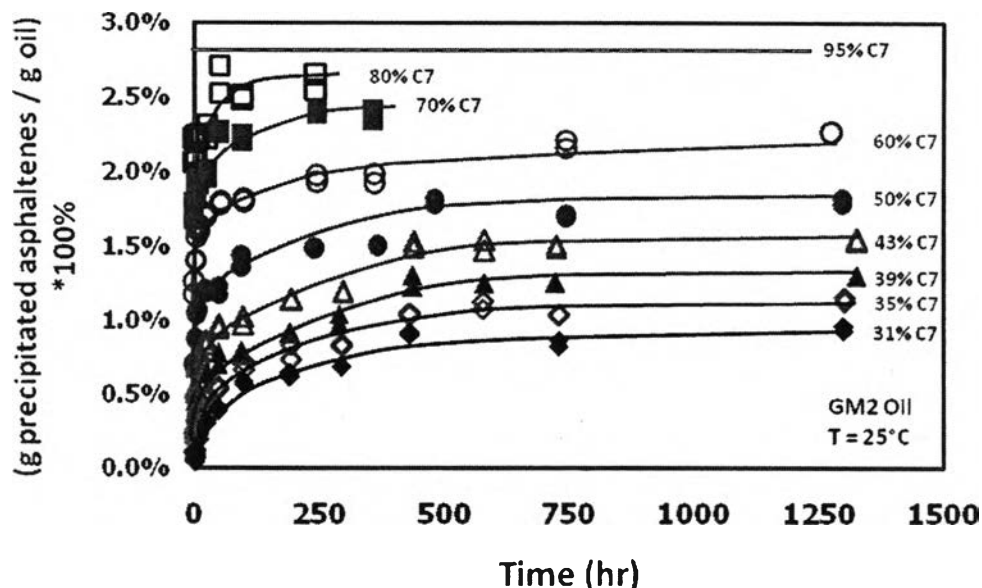


Figure 4.7 Yield of precipitated asphaltenes as a function of time for different heptane vol% in GM2 oil.

The solubility curve for asphaltenes in GM2 crude oil–heptane mixtures is generated and shown in Figure 4.8. This solubility curve represents the equilibrium amount of asphaltenes per mass of crude oil that are soluble in the crude oil–heptane mixture. It shows that as heptane vol% decreases, the mass of soluble asphaltenes per mass of crude oil increases until it reaches the total amount of soluble asphaltenes in the crude oil.

Most researchers measured the amount of precipitated asphaltenes using a the conventional waiting time of only up to 24 hours (Alboudwarej, *et al.*, 2003; Wiehe, *et al.*, 2005; de Sousa, *et al.*, 2004). More importantly, short–term experiments have been used to validate the thermodynamic models they have proposed (Wang & Buckley, 2003; Alboudwarej, *et al.*, 2003; Garcia & Corraera, 2007; Donaggio, *et al.*, 2001; Cimino, *et al.*, 1995; Mohammadi, *et al.*, 2008). However, it has been established that it can take days, weeks or even months to reach the equilibrium amount of precipitated asphaltenes. Figure 4.9 clearly shows that short-term experiments significantly overpredict the amount of soluble asphaltenes in the crude oil.

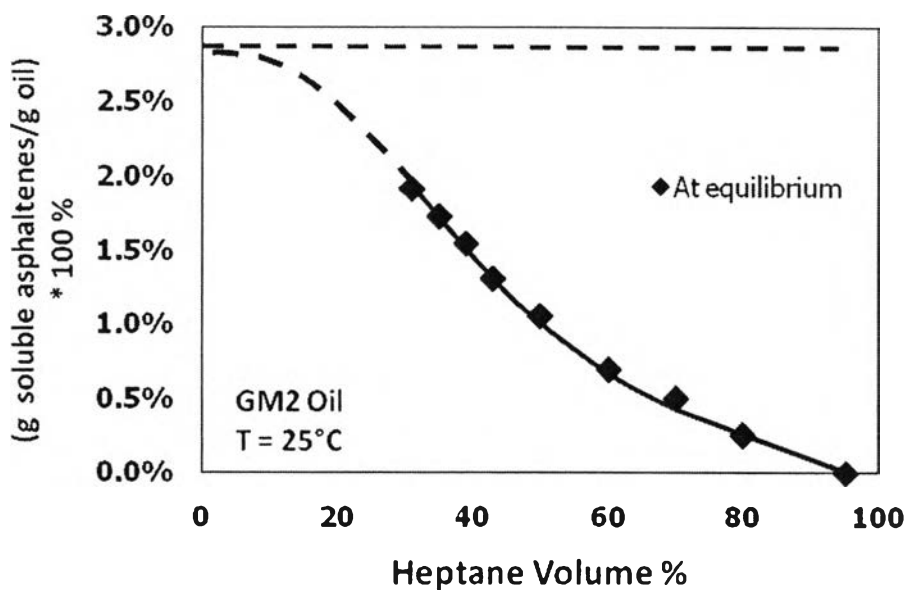


Figure 4.8 Solubility of asphaltenes in GM2 oil as a function of heptane concentration.

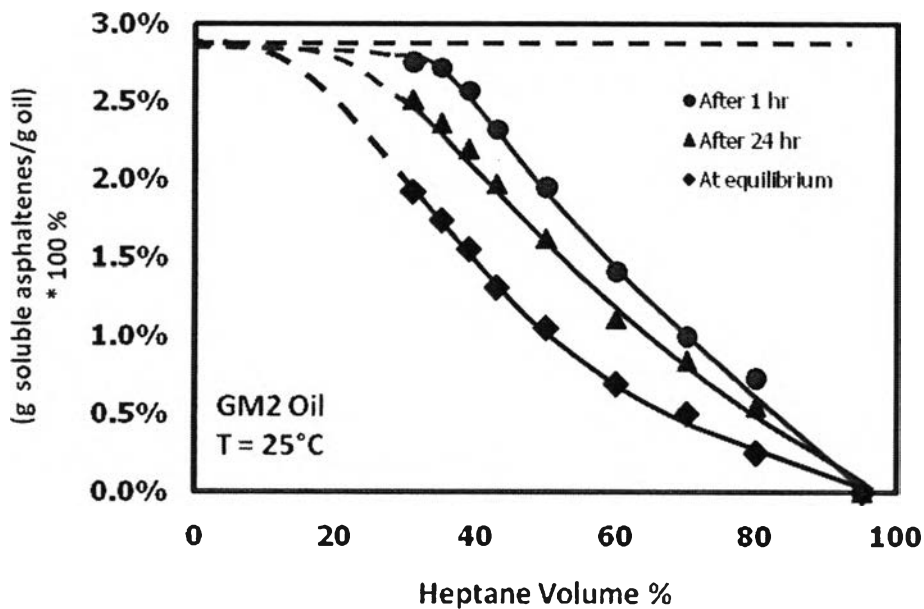


Figure 4.9. Solubility curve for precipitated asphaltenes in GM2 oil as a function of heptane concentration at different waiting times.

4.5 Application of the Geometric Population Balance Model

The geometric population balance model using the Brownian flocculation kernel was validated with the experimental results from centrifugation experiments for GM2 oil using n-heptane as a precipitant. Since the model assumes the aggregation of destabilized asphaltenes from its primary particle size (1.5 nm) to micron size, it is only applied for heptane concentrations at and below instantaneous precipitation.

Figure 4.10 shows the comparison of the simulation and experimental results for the 31 volume % heptane mixture. The model predicts the gradual increase in the yield of precipitated asphaltenes until it plateaus to the equilibrium yield.

The collision efficiency, β is optimized by minimizing the least-square errors between experimental data and simulation results. β is the only fitting parameter used in the model. For the 31 vol% heptane, $\beta = 1.55 \times 10^{-8}$ which means that out of β^{-1} (i.e. 6.44×10^7) number of collisions, 1 will be successful and aggregation will occur. Figure 4.11, 4.12 and 4.13 show the simulated and experimental results for 35, 39 and 43 volume % heptane, respectively. The corresponding collision efficiencies, β are 1.71×10^{-8} , 1.78×10^{-8} and 2.62×10^{-8} , respectively.

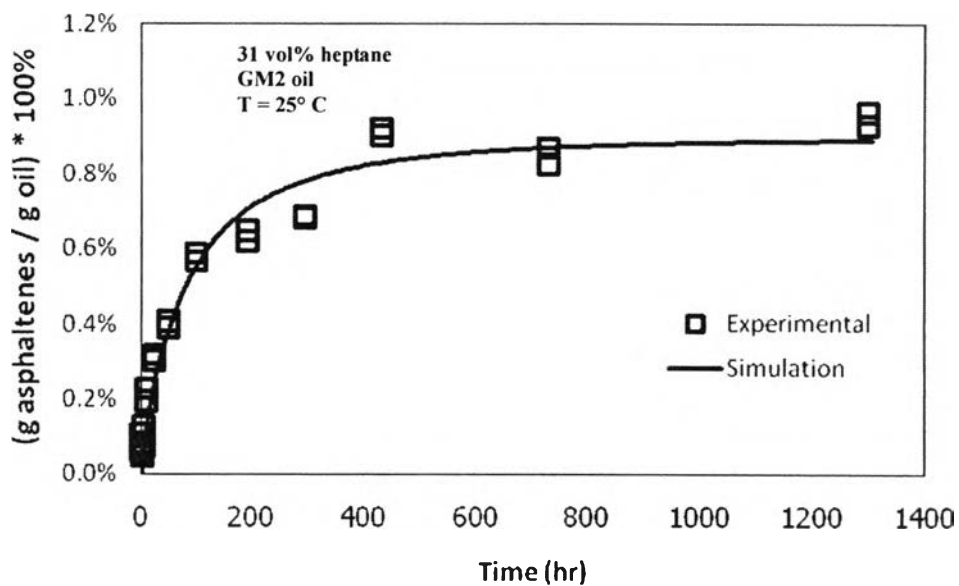


Figure 4.10 Experimental and simulation results for the evolution of separated asphaltene aggregates for 31 vol% heptane in GM2 oil.

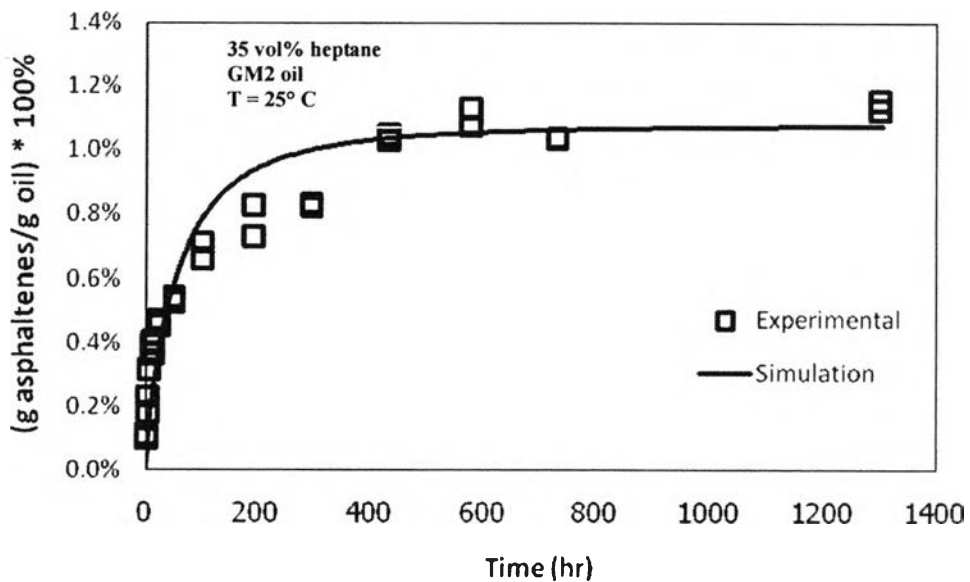


Figure 4.11 Experimental and simulation results for the evolution of separated asphaltene aggregates for 35 vol% heptane in GM2 oil.

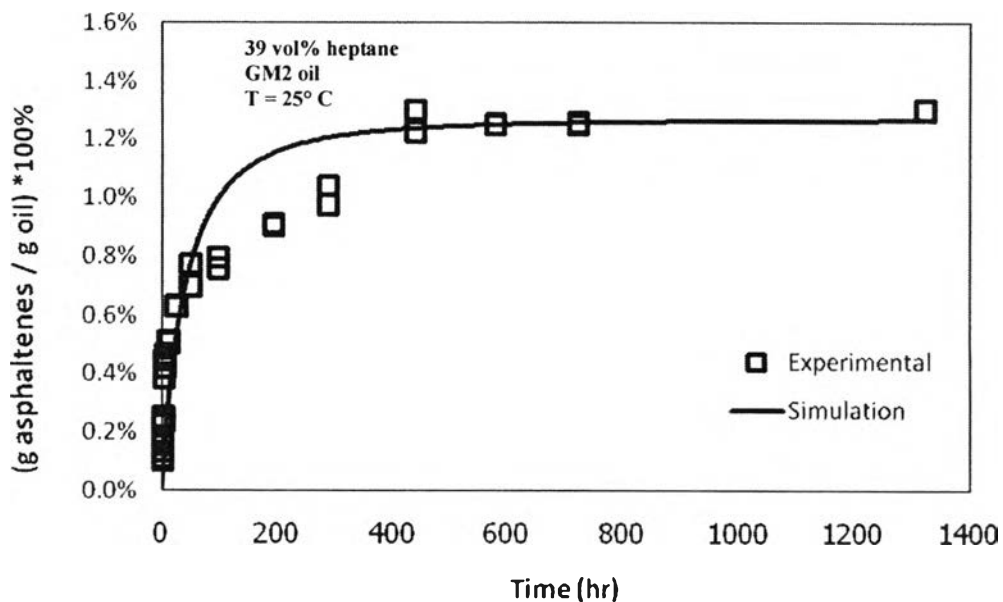


Figure 4.12 Experimental and simulation results for the evolution of separated asphaltene aggregates for 39 vol% heptane in GM2 oil.

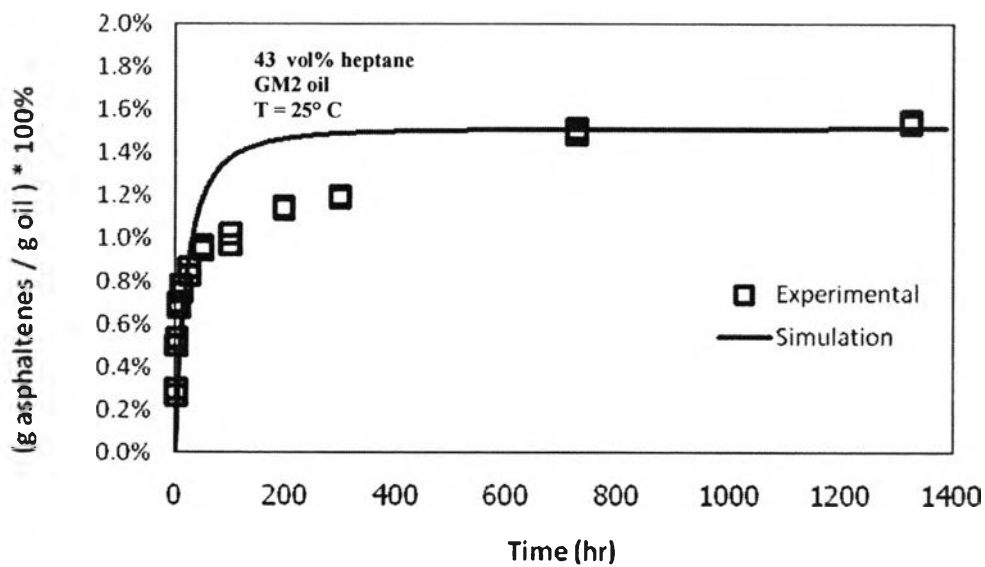


Figure 4.13 Experimental and simulation results for the evolution of separated asphaltene aggregates for 43 vol% heptane in GM2 oil.

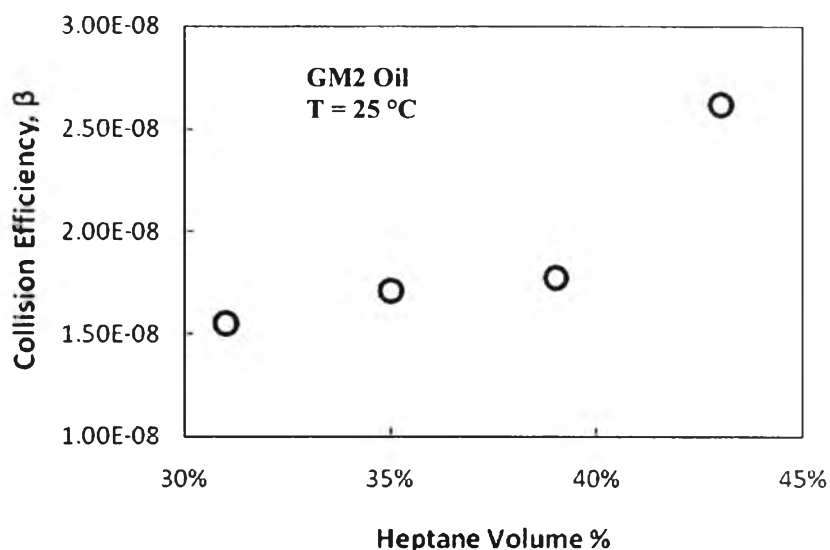


Figure 4.14 Collision efficiency for different heptane volume % in GM2 oil.

Figure 4.14 shows that as the heptane volume % increases, the collision efficiency also increases. As the heptane vol% increases, the number of destabilized asphaltenes also increases and the collision efficiency between destabilized asphaltenes increases leading to faster aggregation.

Additionally, as the heptane concentration increases, the viscosity of the mixture decreases. The reduction in medium viscosity also increases the collision frequency between asphaltene aggregates. Thus, the aggregation of asphaltenes accelerates with the increase in heptane concentration.

The kinetics of asphaltene precipitation has been described by the aggregation of destabilized asphaltenes using the geometric population balance.

4.6 Effect of the type of n-alkane on the kinetics of asphaltene precipitation

Different n-alkanes ranging from n-hexane to n-pentadecane were used to induce precipitation of asphaltenes from GM2 oil. The precipitating power of each n-alkane at high dilution ratio of 1 (oil) : 40 (precipitant) has been demonstrated by mixing crude oils with n-alkane (Speight, 2007) as shown in Figure 2.2. At this high dilution ratio, as the chain length of the n-alkane increases, the yield of precipitated

asphaltenes decreases. The motivation of using high dilution ratio with n-alkane is to overwhelm the system with the precipitant, precipitate all the asphaltenes that can be separated by the n-alkane and determine the yield of precipitated asphaltenes. However, at low dilution ratios of different n-alkanes (i.e. precipitant concentrations at or below instantaneous precipitation), the least soluble asphaltenes can be initially precipitated and can be studied in terms of precipitation onset time.

Figure 4.15 shows similar kinetic trends on asphaltene precipitation that was established for n-heptane. As the precipitant volume % decreases, the precipitation onset time increases exponentially. Figure 4.16 shows the effect of the type of n-alkane precipitant on the precipitation onset time. On a volume % basis using different n-alkane precipitants, the precipitation onset time increases from n-hexane to n-nonane and then decreases to n-pentadecane.

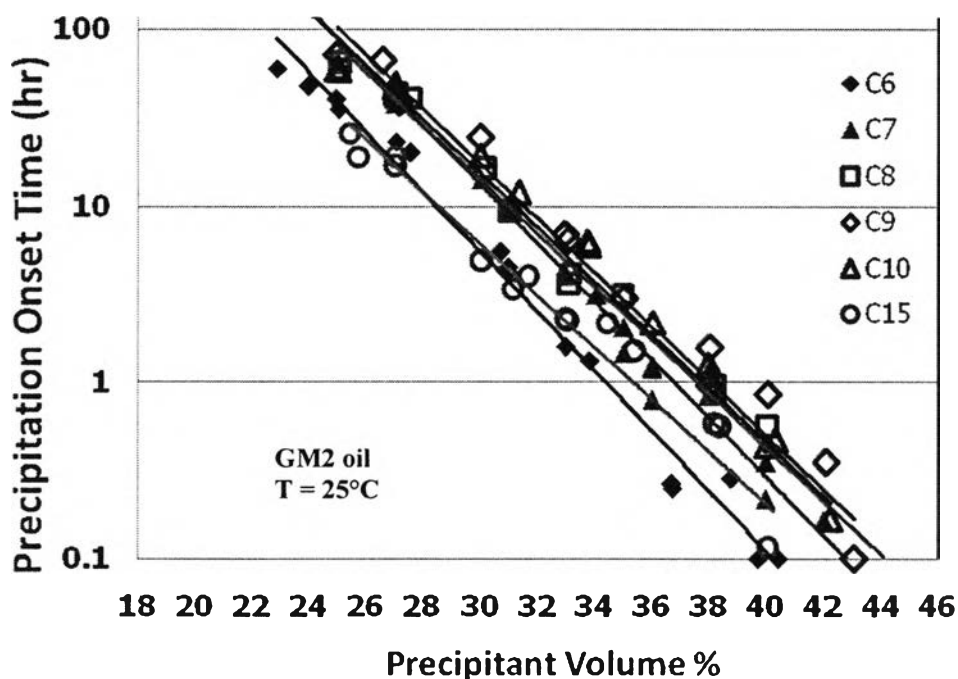


Figure 4.15 Precipitation onset time vs. precipitant volume % for different n-alkanes on a semi-log plot.

The results shown in Figure 4.17 are consistent with Wang and Buckley's (2001) work even though their waiting time was only 24 hours. As the chain length of the n-alkane precipitant increases, the required volume to induce

precipitation increases and reaches a maximum for n-octane to n-decane, and decreases until n-pentadecane.

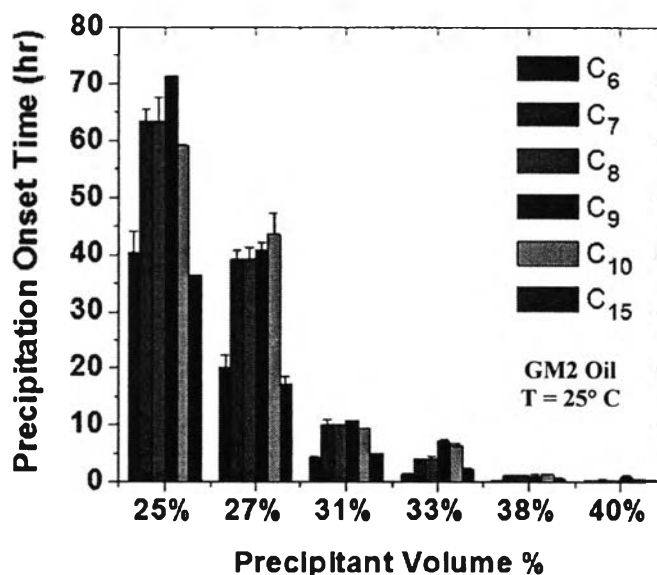


Figure 4.16 Precipitation onset time vs. precipitant volume % for different n-alkanes on a column graph.

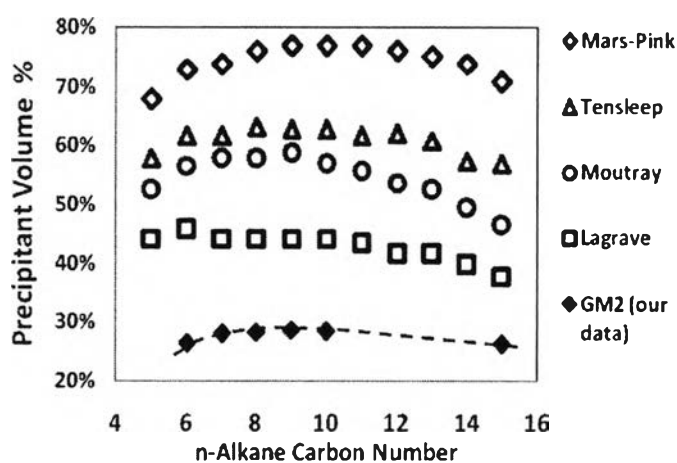


Figure 4.17 Precipitant vol% required to induce asphaltene precipitation after 24 hour waiting time using different n-alkanes. (Adapted from Wang and Buckley, 2001)

However, kinetic effects are significant for asphaltene precipitation. It is shown in Figure 4.18 that the required amount of precipitant for asphaltene precipitation varies with different waiting times. This observation reiterates that the approach of using a conventional waiting time is an experimental artifact.

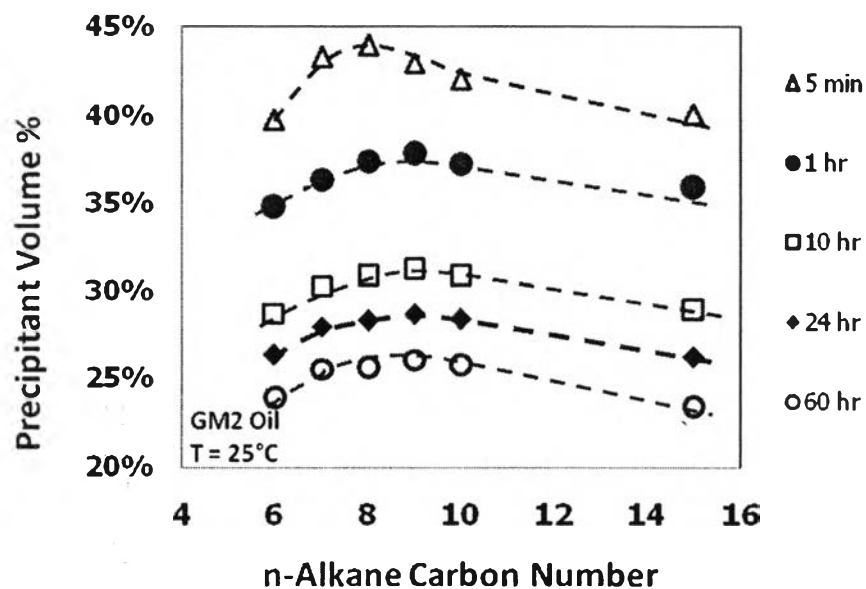


Figure 4.18 Precipitant vol% required to induce asphaltene precipitation at different waiting times using different n-alkanes for GM2 oil.

Wiehe, *et al.* (2005) conducted similar precipitation onset experiments, replotted their results on a molar basis and observed no maximum similar to Figure 4.19. Figure 4.15 was re-plotted on a molar basis as shown in Figure 4.20 and showed that for a particular precipitant mole %, the precipitant onset time decreases as the n-alkane carbon number increases. However, since this system of asphaltenes in crude oil and n-alkanes is non-ideal, the appropriate basis to use would be the volumetric basis. (See Appendix H)

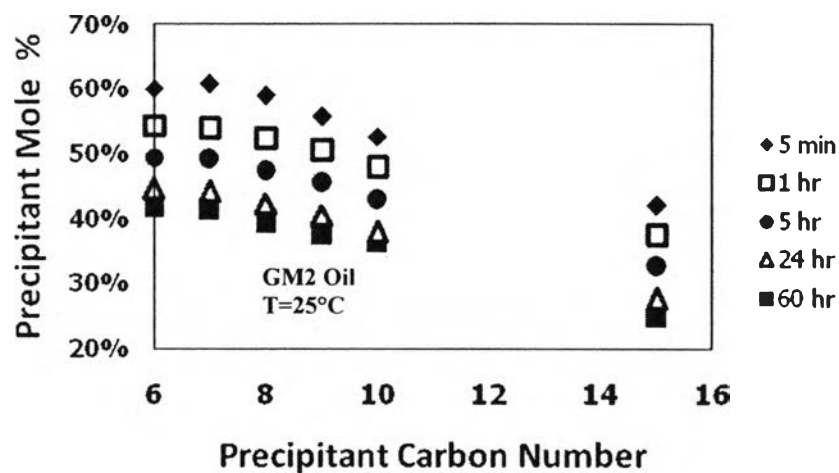


Figure 4.19 Precipitant mole % required to induce asphaltene precipitation at different waiting times using different n-alkanes for GM2 oil.

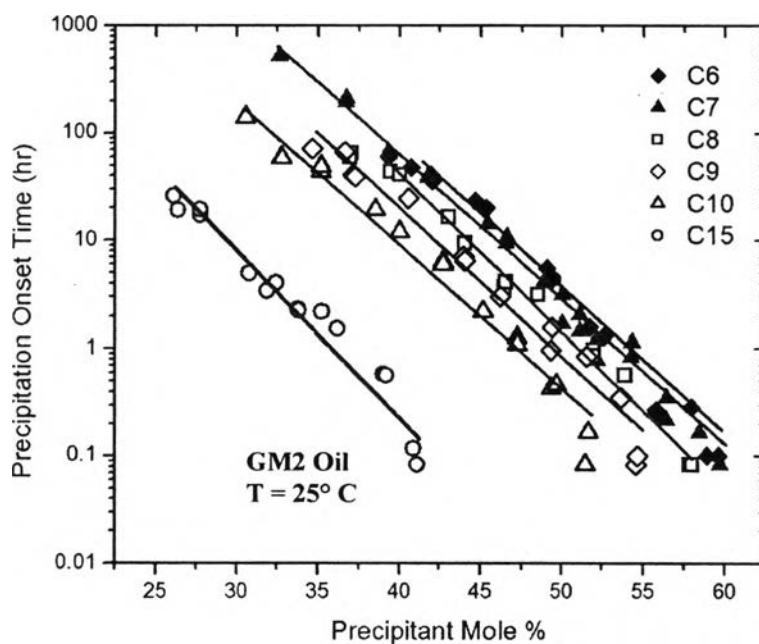


Figure 4.20 Precipitation onset time vs. precipitant mole % for GM2 oil using different n-alkane precipitants.

4.7 A hypothesis on the effect of the type of n-alkane on the kinetics of asphaltene precipitation

Since asphaltenes are a distribution of polydisperse, complex molecules, different fractions of these molecules would have different properties and would tend to behave differently with the surrounding medium in the oil mixture. Creek (2005) showed that asphaltenes is a broad spectrum of species, as indicated by the molecular weight distributions by size exclusion chromatography.

Fuhr, *et al.* (1991) precipitated asphaltenes using different n-alkanes (n-pentane, n hexane, n-octane, n-nonane) at a dilution ratio of 10:1 (precipitant:oil). They analyzed the precipitated asphaltenes with regards to their molecular weight by vapor pressure osmometry (VPO) and aromaticity by NMR and found a general increasing trend on the molecular weight and the aromaticity of the asphaltenes as the carbon number of the n-alkane precipitant increases. This observation suggests that there are differences in the chemical properties of asphaltenes precipitated by different n-alkanes. Moreover, Fuhr, *et al.* (1991) concluded that the lowest solubility (i.e. least stable) precipitated asphaltenes are those with the highest molecular weight and aromaticity. Aromaticity has been referred to as the relative amount of the aromatic carbon to the total carbon (Ouchi, 1985). Also, asphaltenes with high heteroatom content indicated high propensity to precipitation (Daaou, *et al.*, 2008).

Based on Speight's (2007) studies, as the carbon number of the n-alkane increases, the yield of precipitated asphaltenes decreases (Figure 2.2). Long chain n-alkanes precipitate the least fraction of the asphaltene distribution. Since the least stable asphaltenes always precipitate first (Buckley, *et al.*, 2007), it suggests that the long chain alkanes precipitate the least stable (i.e. high instability) fraction of the asphaltene distribution. Moreover, as the carbon number of the alkane decreases, the yield of precipitated asphaltenes increases, suggesting that short alkane chains precipitate a wider spectrum of the asphaltene distribution as seen in Figure 4.21.

It is hypothesized in Figure 4.21 that different n-alkanes would separate different fractions of the asphaltene distribution that have different properties. N-Pentadecane would precipitate the least amount of asphaltenes but with the highest molecular weight and aromaticity, which resembles the least stable fraction of the

distribution. On the other hand, since n-hexane has precipitated a wider spectrum of asphaltenes, C6-asphaltenes would have an average MW and aromaticity of the precipitated spectrum. After addition of the precipitant, asphaltenes are destabilized instantaneously. However, different n-alkanes would destabilize asphaltenes with different degrees of instability. The least stable asphaltenes would have the highest tendency to aggregate and the highest collision efficiency, as described in Figure 4.22.

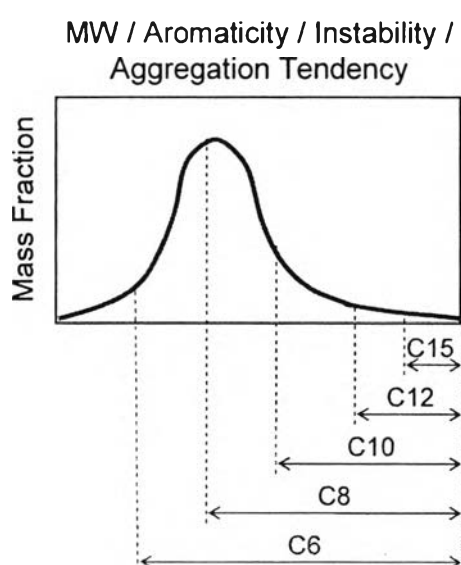


Figure 4.21 Hypothetical asphaltene distribution and the fractions precipitated by different n-alkanes

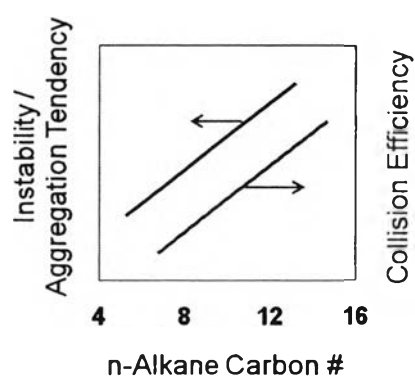


Figure 4.22 Instability, aggregation tendency and collision efficiency of asphaltenes precipitated by different n-alkanes.

However, the viscosity of the n-alkane–crude oil medium hinders the aggregation of destabilized asphaltenes. The viscosity of the medium increases as the alkane chain length increases, which can decrease the frequency of collisions between destabilized asphaltenes, as shown in Figure 4.23. Thus, using n-hexane would make the medium least viscous and increase the collision frequency between unstable asphaltenes.

Because of the competing effects between the collision efficiency and the collision frequency between destabilized asphaltenes, the rate of aggregation can reach a minimum for medium chain alkanes, as described in Figure 4.24. This hypothesis could describe the phenomenon that as the precipitant chain length increases, the precipitation onset time increases, reaches a maximum at medium alkane chain length, and decreases for long chain alkanes, as seen in Figure 4.16. However, this hypothesis needs to be validated by characterization experiments that would investigate the aggregation tendency of asphaltenes precipitated by different n-alkanes. Aromaticity, heteroatom content, or polarity are the factors, which may affect the aggregation tendency of asphaltenes.

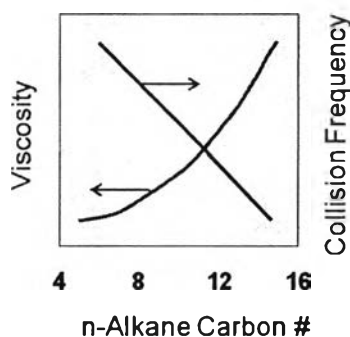


Figure 4.23 Effect of the medium viscosity on the collision frequency of destabilized asphaltenes.

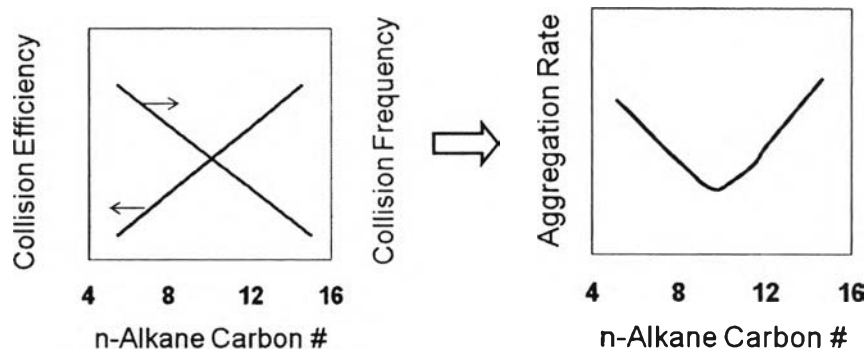


Figure 4.24 Competing effects of collision efficiency and collision frequency which affects the rate of aggregation of destabilized asphaltenes.

4.8 Effect of blending different precipitants on the kinetics of asphaltene precipitation

Crude oil blending is a regular occurrence used in the oil industry to decrease the viscosity of heavy crude oils, which allows for easier transportation (Wiehe, 2008). Blending oils is commonly seen with a heavy oil combined with a light oil. However, some oils are incompatible with each other, which may result in instability and precipitation of asphaltenes (Wiehe, 2000). Mixing a light paraffinic oil with a heavy oil will increase the amount of saturates in the blend of crude oils and precipitate the asphaltenes.

Light crude oils consist of different fractions of saturates which act as “precipitants”. Mixing a crude oil with a blend of different n-alkanes can be used to imitate the blending of incompatible oils. Experimental results from this initial study contributed to the general understanding of the kinetics of asphaltene precipitation when incompatible oils are blended.

Different concentrations of n-hexane and n-octane precipitants were mixed to make a blend of hexane : octane 1:3, 1:1 and 3:1. The blends are mixed with GM2 oil and the precipitation onset time is monitored for 33 vol%, 31 vol% and 27 vol% of precipitant. Figure 4.25 shows the precipitation onset time for a system of 33 vol % of precipitant for different blends. For a 33 vol% precipitant mixture, pure n-hexane precipitates asphaltenes with a precipitation onset time of 1.5 hr while pure

n-octane has a precipitation onset time of 3.8 hr. For a 3 hexane : 1 octane blend, the precipitation onset time does not vary much as compared to using pure hexane. As the octane fraction of the blend increases linearly, the precipitation onset time increases but not a linear fashion. Other precipitant concentrations also show the similar trend (Figure 4.26 and 4.27). It is demonstrated that the relationship between the fraction of the precipitant in a blend and the precipitation onset time is not volume averaged since the experimental results do not lie on the straight dash line. Even though the precipitation onset time is plotted on a log scale, the relationship is still not linear. These results have shown that the stronger precipitant governs the kinetic behavior of the blend. This observation can be extended to blending of crude oils by determining the saturates composition of the oil. The relative amounts of the saturate fractions could indicate which fraction would govern in the kinetic behavior.

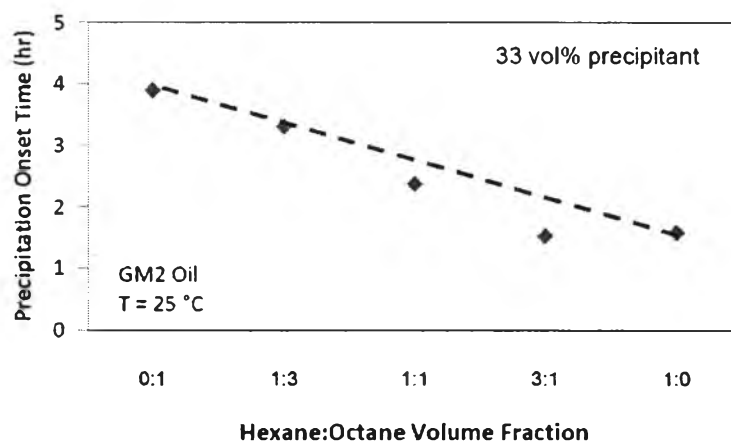


Figure 4.25 Precipitation onset time of 33 vol% hexane-octane blend precipitant in GM2 oil.

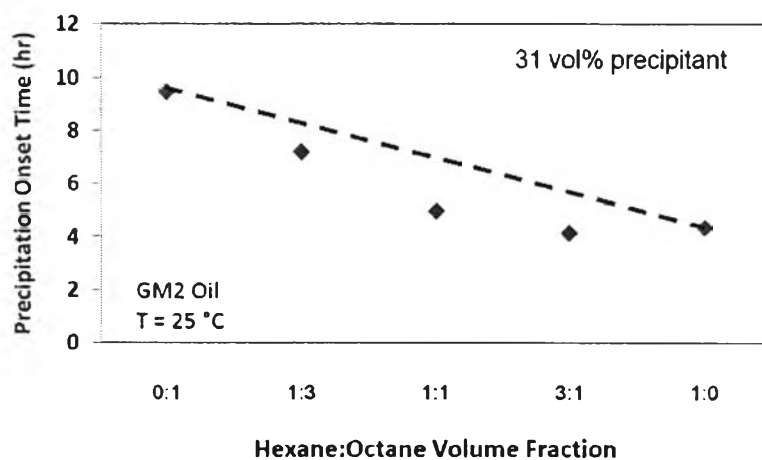


Figure 4.26 Precipitation onset time of 31 vol% hexane-octane blend precipitant in GM2 oil.

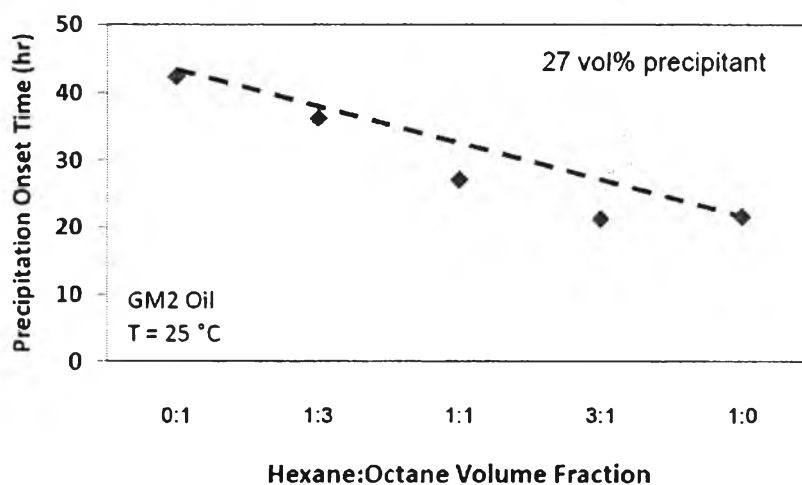


Figure 4.27 Precipitation onset time of 27 vol% hexane-octane blend precipitant in GM2 oil.