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APPENDICES

APPENDIX A: **Difference between asphaltenes and water bubbles as seen under the microscope**

Asphaltenes are opaque particles while water bubbles are transparent as seen under the microscope. However, a correct adjustment of the focus of the microscope is necessary to differentiate between the asphaltenes and water bubbles. After sharply focusing the edge of the sample drop, asphaltenes appear as dark opaque particles with irregular shape while water bubbles are clear and have a round shape as shown in Figures A.1 and A.2.
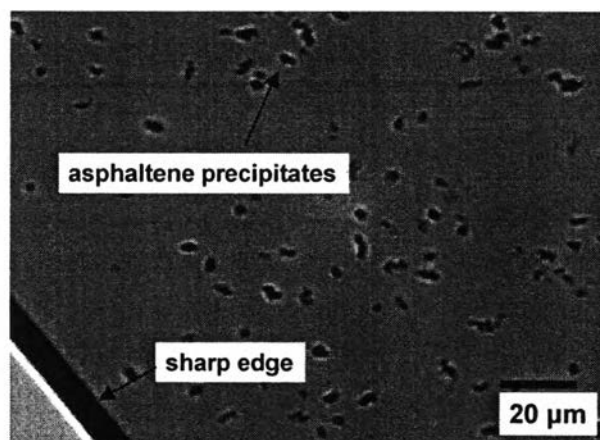
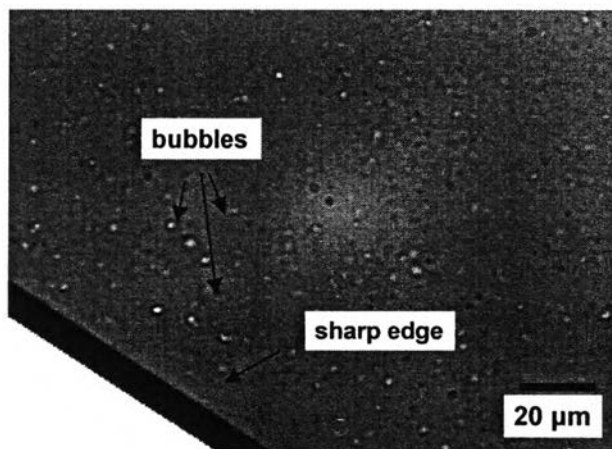**Figure A.1** Image of asphaltene precipitates under 500x magnification.

Figure A.2 Image of bubbles under 500x magnification.

Upon adjusting the focus of the microscope, asphaltenes change their appearance from dark opaque particles to bright particles with a hazy outline as shown in Figure A.3. However, water bubbles change from clear to dark particles. Figure A.4 shows the images captured after adjustment of the focus counterclockwise from the original position. Without the right focus, water bubbles may be misinterpreted as asphaltene particles.
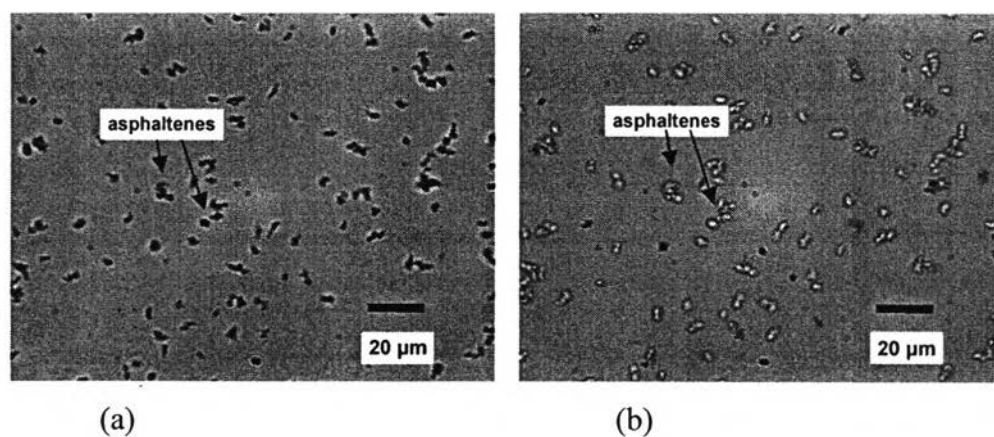

(a)

(b)

Figure A.3 Image of asphaltenes in crude oil at the (a) correct focus, (b) wrong focus.

(a)

(b)

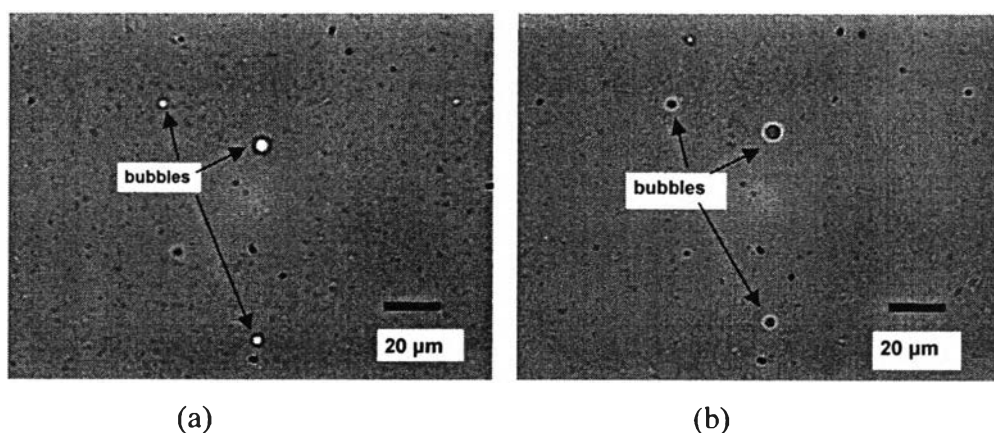**Figure A.4** Image of bubbles in crude oil at the (a) correct focus, (b) wrong focus.

APPENDIX B: **Change in kinetic behavior of N2 crude oil**

N2 crude oil was initially stored in its original steel drum container. The drum was shaken vigorously before sampling is done. Then, the sample crude oil was centrifuged and stored into sealed clear glass containers. Onset of precipitation and centrifugation experiments were done and repeated after a few months.

B.1   Precipitation onset time

Experiments regarding the determination of the onset of precipitation were repeated at a later date, after completion of the initial onset curve. However, it was surprising to find that the kinetic behavior of the N2 crude oil has changed. This was a very disturbing finding with a root cause that can be traced from the poor storage conditions of the crude oil. Figure B.1 shows the plot of precipitation onset time for N2 crude oil at different heptane volume %. N2 crude oil that was stored in the laboratory after 3 months showed faster precipitation kinetics.
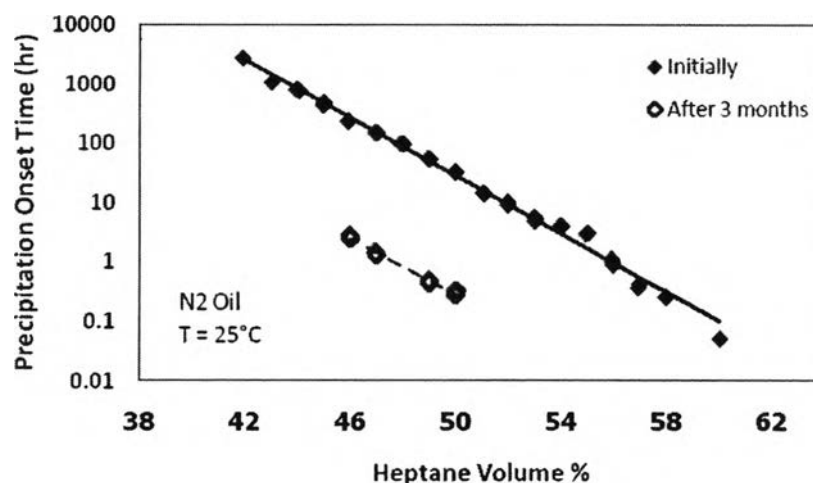
Figure B.1 Precipitation onset time plot at different heptane vol% for N2 crude oil that was used initially and after 3 months of poor storage conditions.

B.2 Quantification of precipitated asphaltene yield as a function of time

In order to check the drastic change in the kinetic behavior of the crude oil sample, centrifugation experiments were also done. Figures B.3 & B.4 show that the aged N2 crude oil had precipitated at a faster rate than the initial N2 crude oil used.
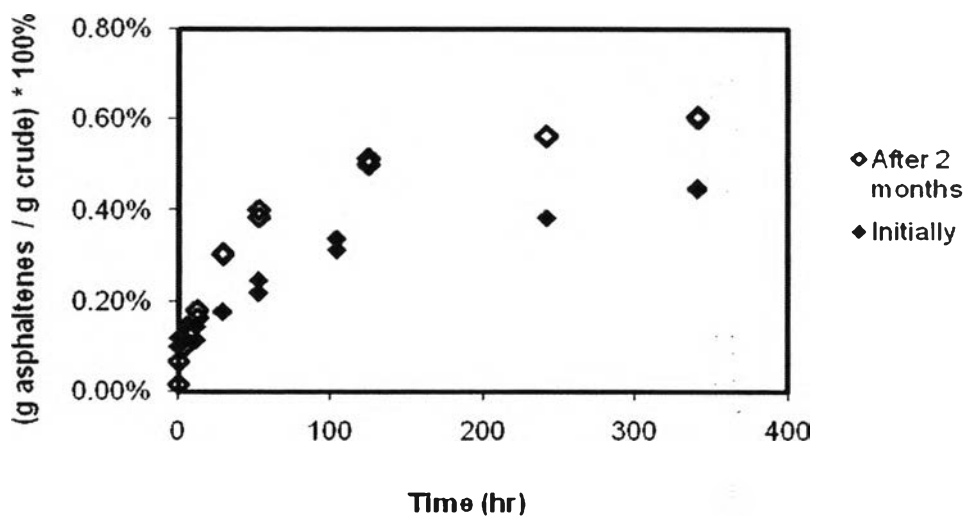

Figure B.2 Centrifugation experiments for 52 vol % heptane in N2 oil initially and after 2 months of poor storage conditions.
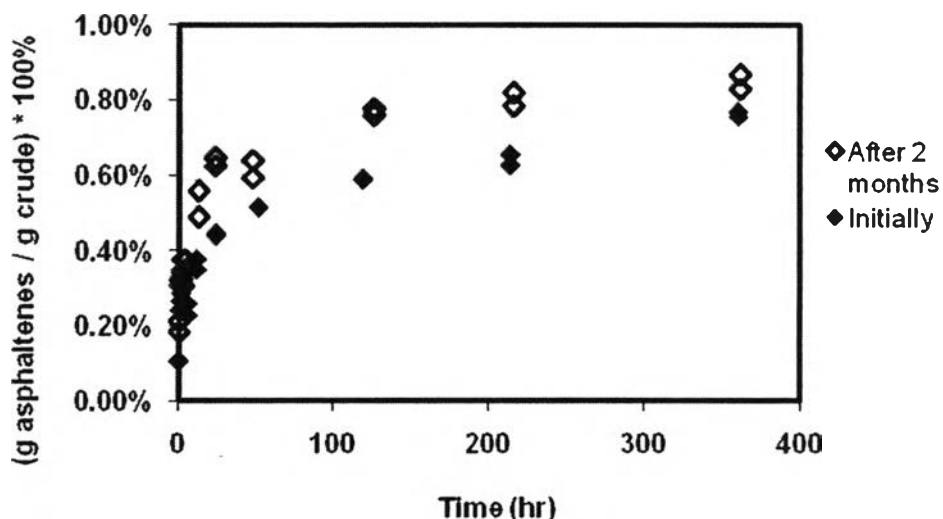

Figure B.3 Centrifugation experiments were done on 56 vol% heptane in N2 crude oil initially and after 2 months of poor storage conditions.

APPENDIX C: **Possible reasons for the change in kinetic behavior of N2 crude oil and preventive measures taken**

The N2 crude oil was stored in its original steel container. Whenever samples are taken from the container, a headspace between the oil surface and top of container is created. This widening headspace provides room for the oil's volatile components to evaporate over time. This evaporation can cause enrichment of the oil with its heavy phase thus, leading to a crude oil richer in asphaltenes. Continuous sampling can lead to further evaporation and further change the oil composition. Frequent opening of the oil container exposes the oil to fresh air which may also cause oxidation.

In order to prevent the changing characteristics of the oil, certain measures were used. Once the crude oil container is opened, the crude oil is transferred to 500mL amber bottles with Poly-Seal™ caps that are purged with inert nitrogen gas. The caps are tightly sealed with electric tape. Crude oils are then kept in room temperature in a dark location inside a box. Whenever samples are required, the entire 500mL oil sample is centrifuged. Centrifuged crude oil is then transferred to nitrogen gas–purged 60mL amber bottles with Poly-Seal™ caps and sealed with Teflon tape. These centrifuged oils are then kept in room temperature at a dark location inside a box.

APPENDIX D: **Reproducibility of results for GM2 oil under proper storage**

A new batch of crude oil, GM2 was studied and the precautionary measures mentioned above were observed. The experiments were successfully reproduced which suggests that the precautionary measures were adequate to maintain the integrity of the crude oil.

D.1   Precipitation Onset Time

Precipitation onset time experiments were successfully reproduced using hexane for GM2 oil as shown in Figure D.1. Reproduced experiments were conducted after 3 months of proper storage conditions. Other experiments using different n-alkanes were also repeated and were successfully reproduced.
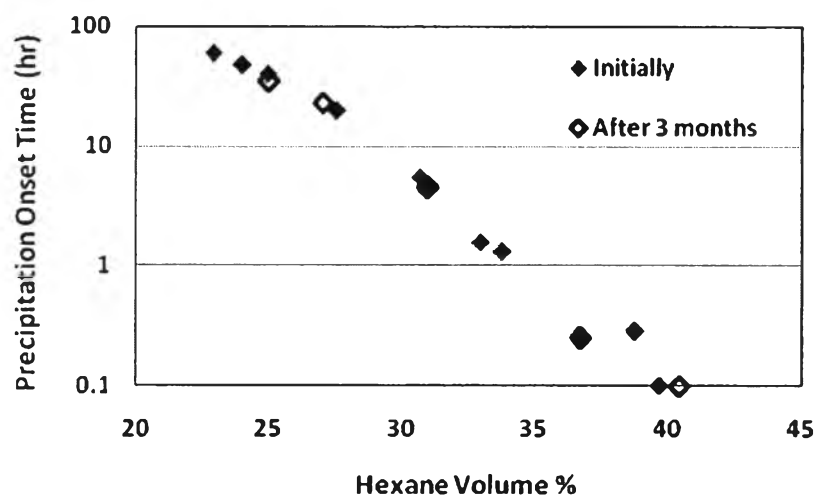

Figure D.1 Reproducibility of results regarding precipitation onset time using n-hexane in GM2 oil.

D.2   Quantification of precipitated asphaltene yield as a function of time

Centrifugation experiments were successfully reproduced for GM2 oil that was properly stored after 3 months. Figure D.2 (a) – (d) shows the successfully

reproduced runs for different heptane concentrations. In order to maintain integrity of the crude oil samples, it is therefore advised to handle and store them with the above-mentioned precautionary measures.
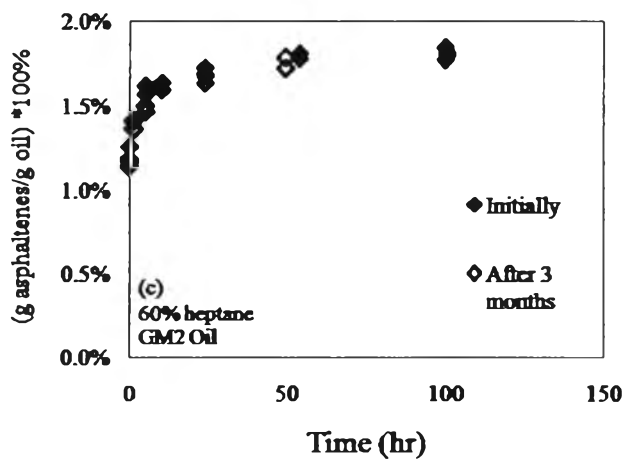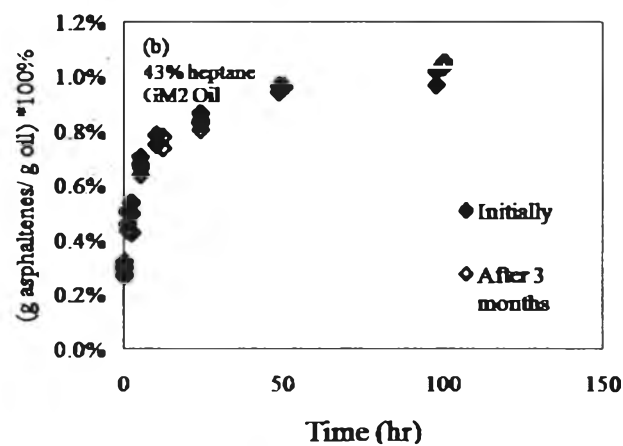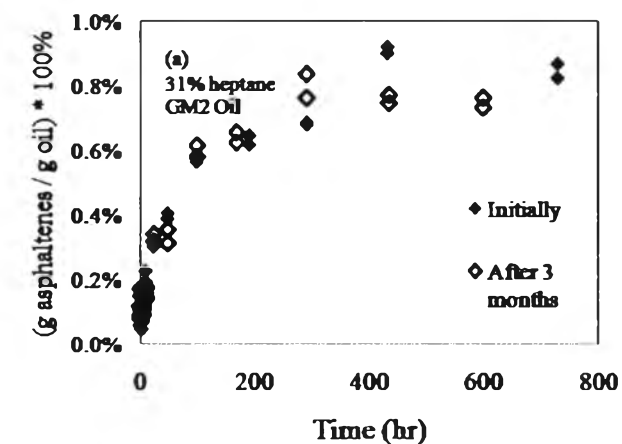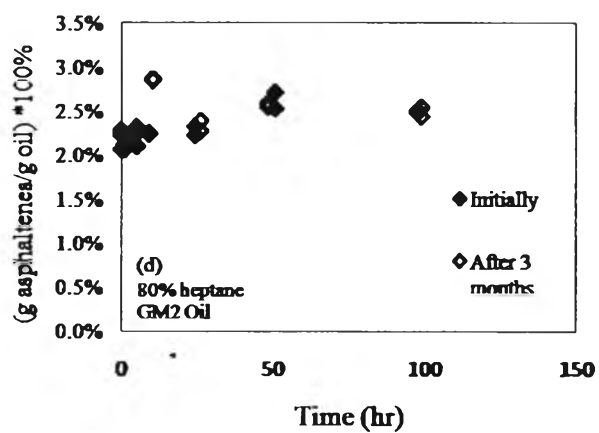
Figure D.2 Reproduced centrifugation runs for GM2 oil at (a) 31, (b) 43, (c) 60 and (d) 80 vol% heptane.

APPENDIX E: **SARA Separation Technique by Baseline Resolution Weatherford Laboratories**

The SARA analysis of GM2 oil was determined by Baseline Resolution Weatherford Laboratories (Walker, 2009). Their SARA separation technique does not follow an ASTM method but rather uses a customized method that can deal better with a wide variety of petroleum types. In general, the crude oil sample is first topped at 60°C under a nitrogen stream to remove the volatile components. Then, the sample is then refluxed using a 30:1 ratio of heptane:crude oil sample for 1 hour. Next, it is placed in a refrigerator for 18 hours. Afterwards, it is removed and filtered through an 8μm filter paper. The filter paper is extracted with clean heptane to remove adsorbed oil and then extracted with dicholoromethane to remove the asphaltenes. A portion of the deasphalted oil is passed through a specially prepared packed silica column using (1) heptane to elute the saturate fraction, (2) toluene to elute the aromatic fraction, and (3) chloroform/methanol to elute the resin fraction. Each of the fraction are then dried and weighed.

The asphaltene content by SARA analysis (3.6%) and centrifugation technique (2.8% ± 0.1%) are different because of the variations in separation techniques used and the treatment of the sample. Baseline's pretreatment procedure which tops the crude oil with flowing nitrogen at 60°C removes the volatile components of the crude oil and makes the oil richer in asphaltene content. Moreover, Baseline uses a filtration technique to separate the precipitated asphaltenes. However, our technique uses a pre-centrifuged crude oil, free from water, sand or impurities. It uses a centrifugation –based separation technique to separate the precipitated asphaltenes.

APPENDIX F: **Preliminary centrifugation results using different n-alkanes**

When n-decane (C_{10}) or n-pentadecane (C_{15}) are used to precipitate asphaltenes, drying is very slow due to their low volatility. Thus, the samples are further washed with n-heptane (C_7) three times to remove any remaining C_{10} or C_{15}. Afterwards, the samples are dried in a vacuum dryer for 12 hours at 25in Hg vacuum at 100°C. The weight of the sample remained constant within ±0.05% between drying time of 6 hr and 12 hr, which suggests that all the precipitant is evaporated.

Relating the thermodynamics and kinetics of asphaltene precipitation, thermodynamics is described by the equilibrium yield of precipitated asphaltenes (i.e. total amount of destabilized asphaltenes) while kinetics is illustrated by the aggregation of destabilized asphaltene nano-aggregates.

Figure F.1 shows the yield of precipitated asphaltenes for a 31 vol% precipitant using hexane, heptane, decane and pentadecane. Based on the preliminary results of these experiments, pentadecane precipitated more asphaltenes than hexane, heptane and decane. This result is contrary to the conventional belief that longer chain alkanes precipitate less fraction of the asphaltenes as studied by Speight (2007). However, Speight's generalization is based on high dilution of precipitant to oil (40:1). Figure F.1 shows the yield of asphaltenes at a low precipitant concentration of 31 vol% with precipitation onset time of around 4 hours for hexane and pentadecane and around 10 hours for heptane and decane. The yield of precipitated asphaltenes follow a trend of pentadecane > hexane > heptane > decane. This result shows that pentadecane has precipitated a higher amount of asphaltenes which may cause faster aggregation of asphaltenes. These results, however, needs to be validated and reproduced. On the other hand, this would be another avenue to pursue in understanding the solubility of asphaltenes in different alkanes at different dilution ratios.
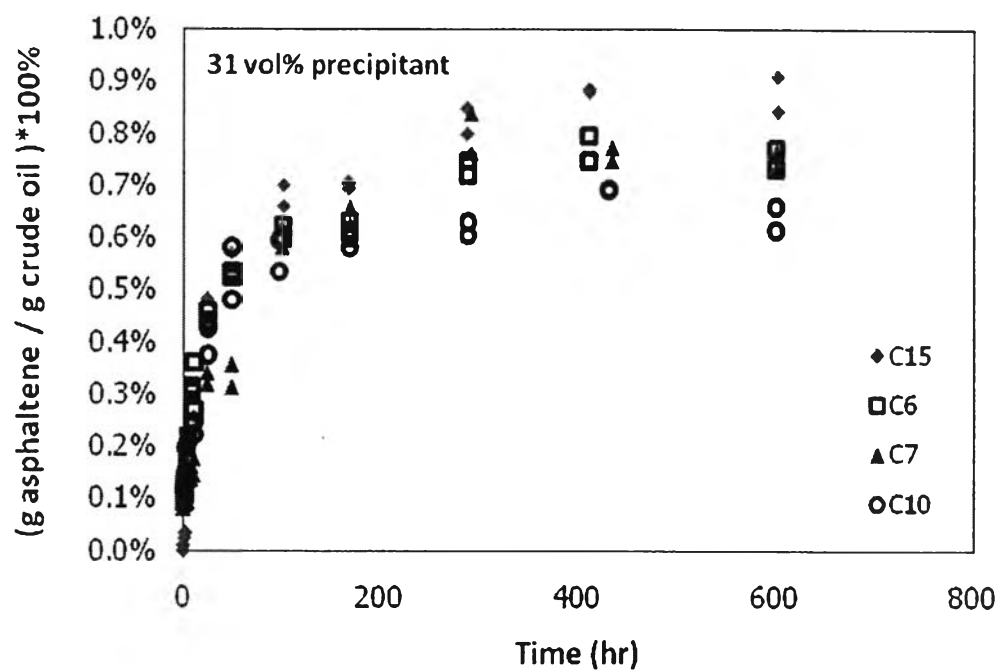
Figure F.1 Yield of precipitated asphaltenes using 31 vol% of precipitant (hexane, heptane, decane and pentadecane).

APPENDIX G: Separation of Particles based on Particle Diameter

A particle that is settling under a centrifugal field is governed by two opposing forces which are the centrifugation force and the drag force. Assuming spherical particles, the summation of forces lead to Equation |A.1| (Allen, 1981).

$$\Sigma \, Forces = \quad (Mass_p)*(acceleration) = \quad Centrifugation \; Force \quad - \quad Drag \; Force$$

$$\frac{\pi}{6}(\rho_p - \rho_f)D^3\frac{d^2x}{dt^2} \;=\; \frac{\pi}{6}(\rho_p - \rho_f)D^3\omega^2x \;-\; 3\pi D\mu\frac{dx}{dt} \qquad (G.1)$$

where: x = distance from the axis to the particle (m)

dx/dt = outward velocity of the particle (m s^{-1})

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

μ = viscosity of fluid medium (kg m^{-1} s^{-1})

D = equivalent spherical diameter of particle (m)

ω = speed of rotation of centrifuge (rad sec^{-1})

At the terminal velocity, the summation of these forces equal zero. Thus, Equation $(G.1)$ becomes

$$\frac{dx}{dt} = \frac{(\rho_p - \rho_f)}{18\mu}D^3\omega^2x \qquad (G.2)$$

$$\int_S^r \frac{dx}{x} = \int_0^{D_m} \frac{(\rho_p - \rho_f)}{18\mu}D^2\omega^2dt$$

$$\ln\frac{r}{S} = \frac{(\rho_p - \rho_f)}{18\mu}D_m^2\omega^2t$$

For r = R which is the bottom of the tube, all particles bigger than D_m are centrifuged.

$$D_m = \sqrt{\frac{18\mu\ln(R/S)}{(\rho_p - \rho_f)\omega^2t}} \qquad (G.3)$$

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

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

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

D_m is calculated based on the physical properties of the particle and the fluid, and the applied centrifugation conditions. D_m serves as a guide if the centrifugation conditions used are sufficient to separate the appropriate particles. Figure G.1 shows the configuration of the centrifuges used.
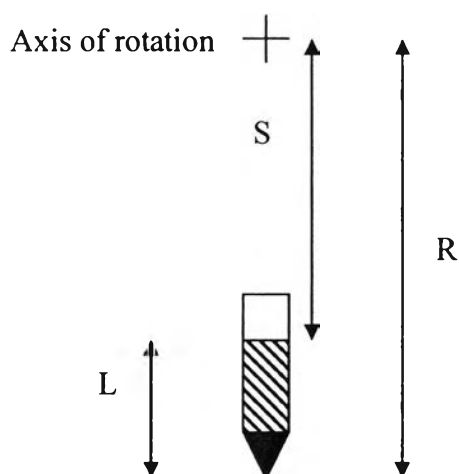

Figure G.1 Configuration of centrifuge used.

Table G.1 Configuration of the centrifuge used

Centrifuge	S (mm)	R (mm)	L (mm)	Centrifuge Tube used
Eppendorf Micro Centrifuge 5415C	39	73	34	Fisherbrand microcentrifuge 1.5mL

APPENDIX H: **Flory-Huggins Theory Describing a System of Dissimilar Molecules**

The Flory-Huggins solution theory is a mathematical model of the thermodynamics of polymer solution which takes into account the differences in the molecular sizes of different species into the entropy of mixing (Flory, 1953). It has been used extensively to model asphaltene precipitation with different n-alkanes (Wiehe *et al.*, 2005; Garcia and Correra, 2007). Asphaltenes and the n-alkanes that are mixed have very different molecular sizes. Therefore, the system is non-ideal and the entropy of mixing is no longer described by Raoult's Law (Flory, 1953).

For a system of molecules of different sizes where the ratio of molar volume of asphaltene and mixture (i.e deasphalted oil and precipitant), $r_{am} = v_a / v_m$ is not equal to 1, the entropy of mixing (Flory, 1953) is

$$\Delta S^M_{F-H} = -R[n_a \ln(\phi_a) + n_m \ln(\phi_m)] \qquad (H.1)$$

where ϕ = volume fraction and

$$\phi_a = \frac{n_a r_{am}}{n_a r_{am} + n_m} \quad , \quad \phi_m = \frac{n_m}{n_a r_{am} + n_m} \qquad (H.2)$$

For molecules of identical molar volumes, $r_{am} = 1$, the Flory-Huggins entropy reduces into an ideal entropy of mixing based on mole fractions. In order to account for the differences in molecular sizes between asphaltenes and the n-alkanes that were used, the entropy of mixing should be based on volume fraction. The volumetric basis is used in interpreting the results of the experiments.

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