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APPENDICES

Appendix A Derivation of Equation (4.2) from Equation (4.1)

From equation (4.1):

$$\delta_{LiveOil} = \phi_{STO}^{RC}\delta_{STO}^{RC} + \phi_{DG}^{RC}\delta_{DG}^{RC} \tag{A.1}$$

$$\delta_{LiveOil} = \frac{V_{STO}^{RC}}{V_{STO}^{RC} + V_{DG}^{RC}}\delta_{STO}^{RC} + \frac{V_{DG}^{RC}}{V_{STO}^{RC} + V_{DG}^{RC}}\delta_{DG}^{RC} \tag{A.2}$$

Let

$$D = \frac{V_{STO}^{RC} + V_{DG}^{RC}}{V_{STO}^{RC}} \tag{A.3}$$

Then equation (A.2) can be rearranged to:

$$\delta_{LiveOil} = \frac{1}{D}\delta_{STO}^{RC} + \frac{1}{D}\frac{V_{DG}^{RC}}{V_{STO}^{RC}}\delta_{DG}^{RC} \tag{A.4}$$

And from molar solubility parameter of dissolved gas (normal alkanes):

$$\delta_{DG}^{RC} = \frac{\delta_{DG}^{M}}{v_{DG}^{RC}} \tag{A.5}$$

Then equation (A.4) can be written as:

$$\delta_{LiveOil} = \frac{1}{D}\delta_{STO}^{RC} + \frac{1}{D}\frac{V_{DG}^{RC}/v_{DG}^{RC}}{V_{STO}^{RC}}\delta_{DG}^{M} \tag{A.6}$$

Let

$$r = \frac{V_{DG}^{RC}/v_{DG}^{RC}}{V_{STO}^{RC}} \tag{A.7}$$

Then equation (A.6) can be written as in equation (4.2) as:

$$\delta_{LiveOil} = \frac{1}{D}\delta_{STO}^{RC} + \frac{r}{D}\delta_{DG}^{M} \tag{A.8}$$

Appendix B Problems with High Pressure System and Solutions

Several problems were found with high pressure system during the test and these problems are shown below:

1. Mixing problem in pressure cell
2. Over-pressured live sample
3. Large dead volume in pressure cell
4. O-ring failure

For mixing problem in pressure cell, a problem was found due to the fluctuation in light transmittance data as shown in Figure B1.

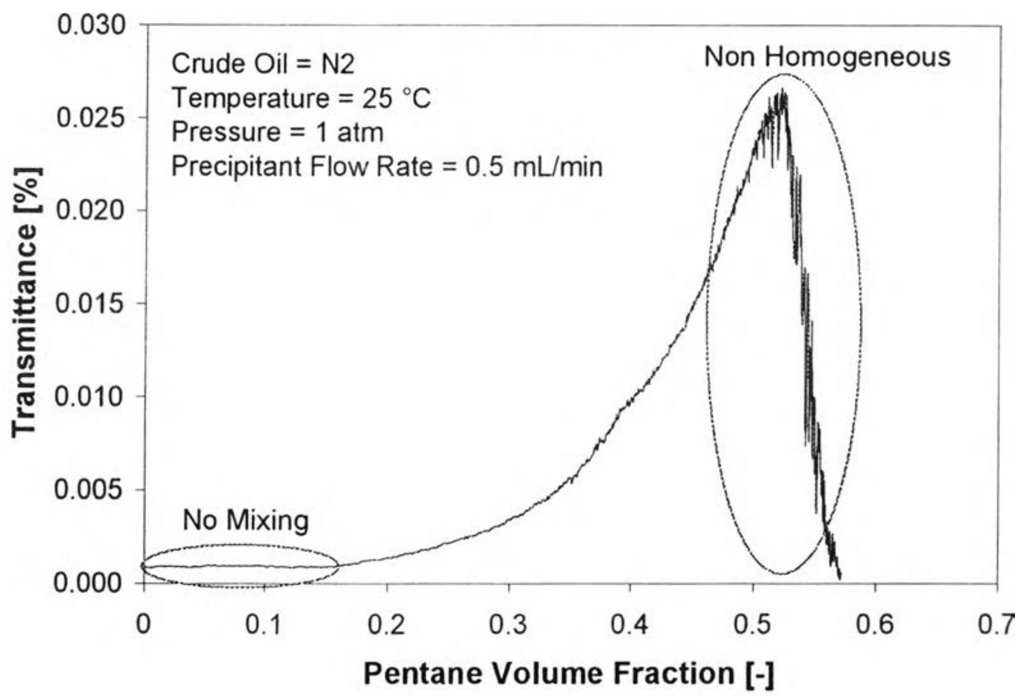

Figure B1 Light transmittance curve showing poor mixing

To fix this problem, several Teflon pieces were added and act as a spacer between the bottom of a magnetic mixer and metal casing. This allowed a magnetic mixer to spin freely and did not rub with metal casing. The modification is shown in

Figure B2. After modification, the light transmittance curve (Figure B3) shows very good mixing with no fluctuation of data.

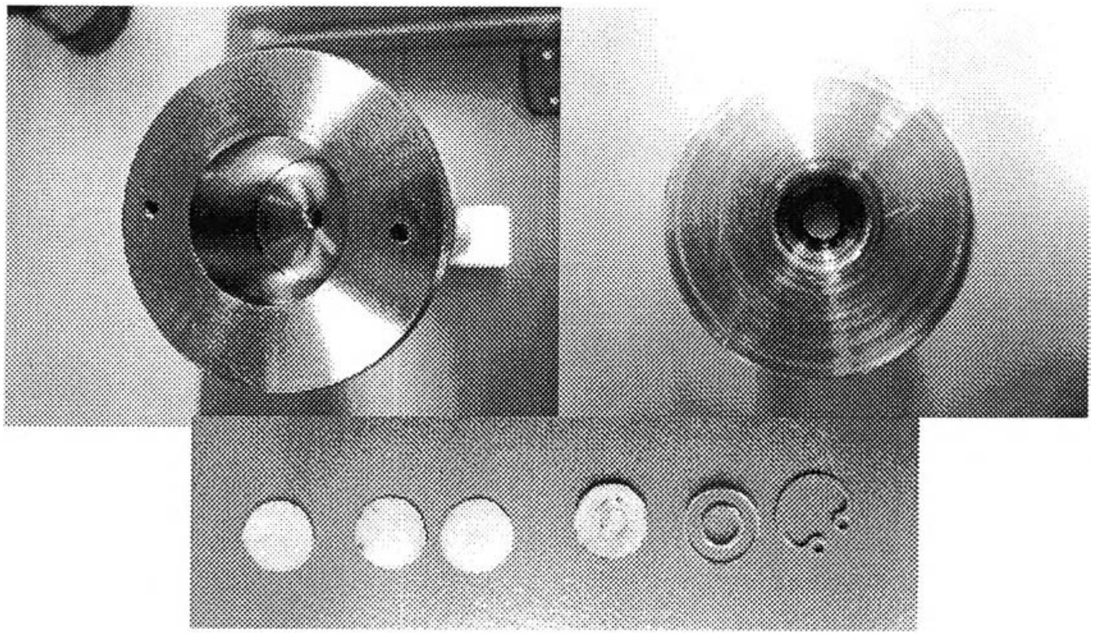

Figure B2 Modification of magnetic mixer

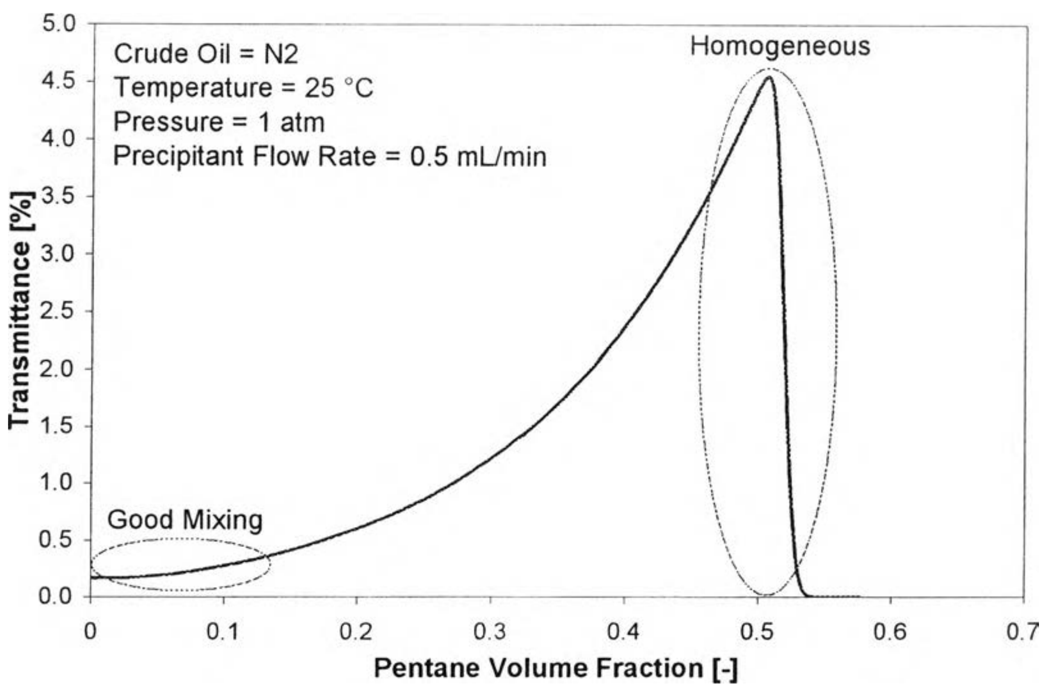

Figure B3 Light transmittance curve showing good mixing after modification

For over-pressured live sample, a live sample received from a third-party company was at 15,000 psi which was high than a pressure that a system can handle. Therefore, a pressure reduction step needed to be performed before the test. Several sections of high pressure tubing (30,000 psi) and a pressure gauge (20,000 psi) were added to the system as shown in Figure B4 and Figure B5. Small amount of mineral oil was released at a time to emptied tubing then expanded to other sections of tubing. These steps were repeated until desire pressure was reached.

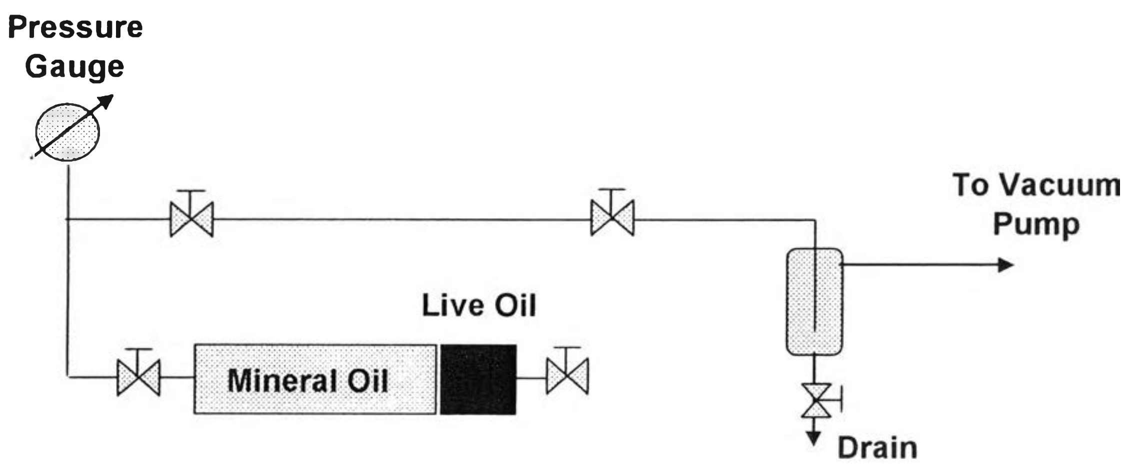

Figure B4 Pressure reduction schematic diagram

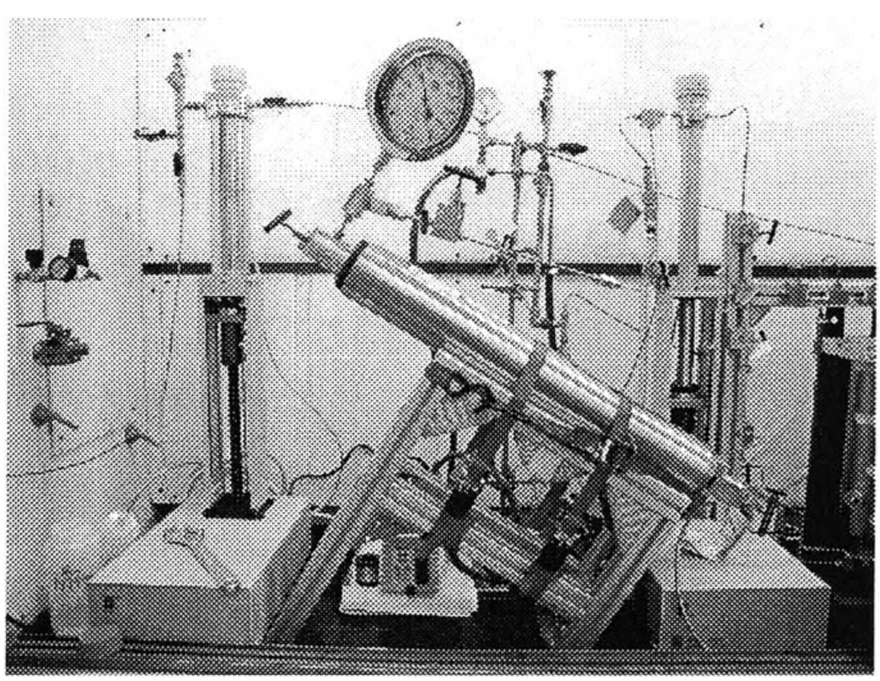

Figure B5 Pressure reduction system

For the dead volume inside the pressure cell, there is about 10-15 mL of dead volume inside the pressure cell from to the original design (Figure B6). This dead volume caused the pressure drop of about 4000 psi for the sample and because mineral oil did not have high expansibility. Therefore, helium was used as a pressure pad on the mineral oil side when introducing the sample because helium have high expansibility and can expand 10-15 mL with less pressure drop.

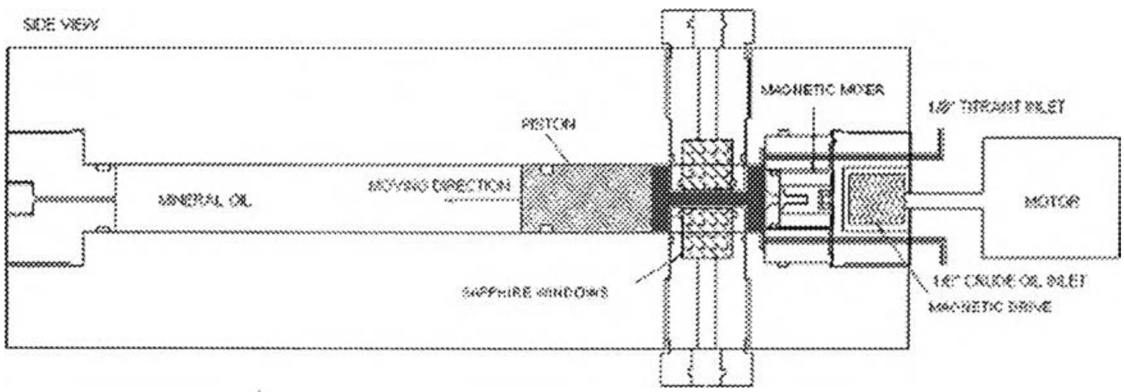

Figure B6 Pressure cell design showing dead volume

Last, o-rings on the sapphire window casings (Figure B7) failed during the test of the system. Therefore, different o-ring elastomers were investigated and tested at high pressure and high temperature. These o-ring elastomers are Nitrile, Aflas, and Viton. Nitrile and Aflas o-rings failed after 40 minutes at 9000 psi and 70 °C with mineral oil and live oil shown in Figure B8 and Figure B9. Viton o-rings passed the test at 9000 psi and 70 °C with mineral oil and live oil shown in Figure B10. Therefore, Viton o-rings were chosen for all future tests.

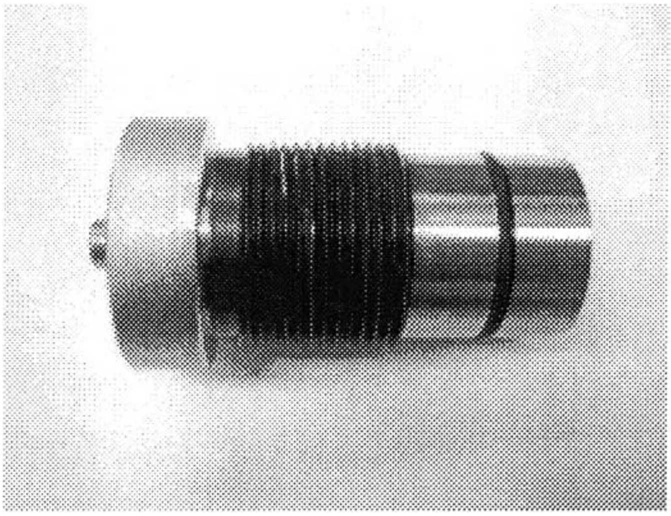

Figure B7 O-ring on sapphire window casing

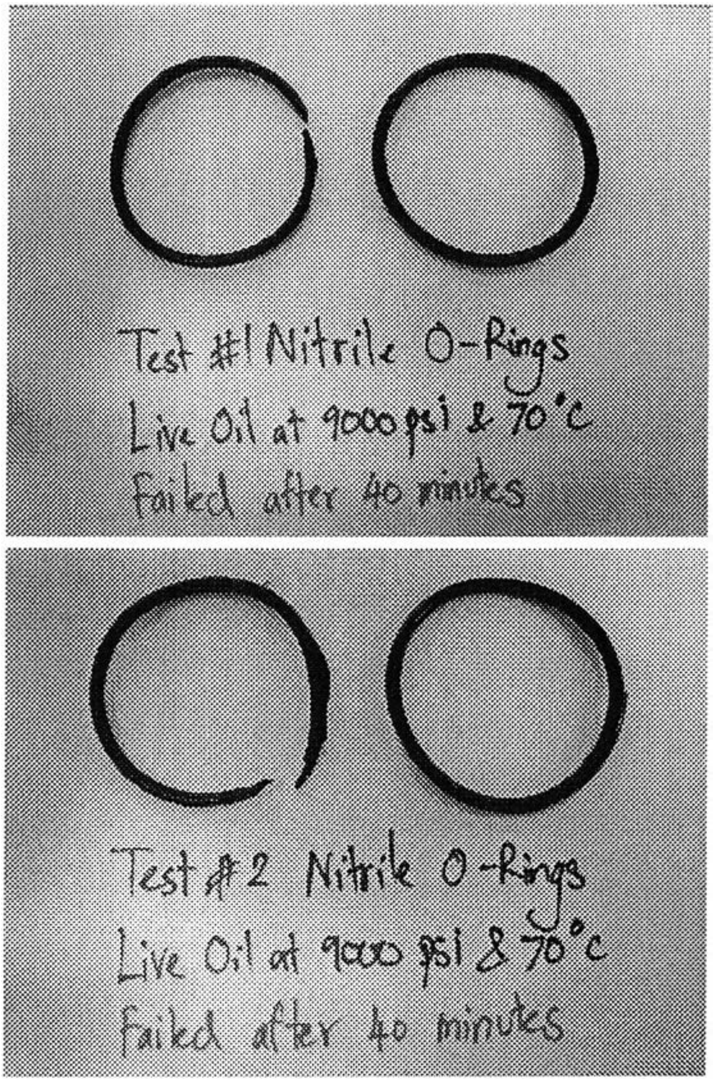

Figure B8 Nitrile o-rings failed after 40 minutes

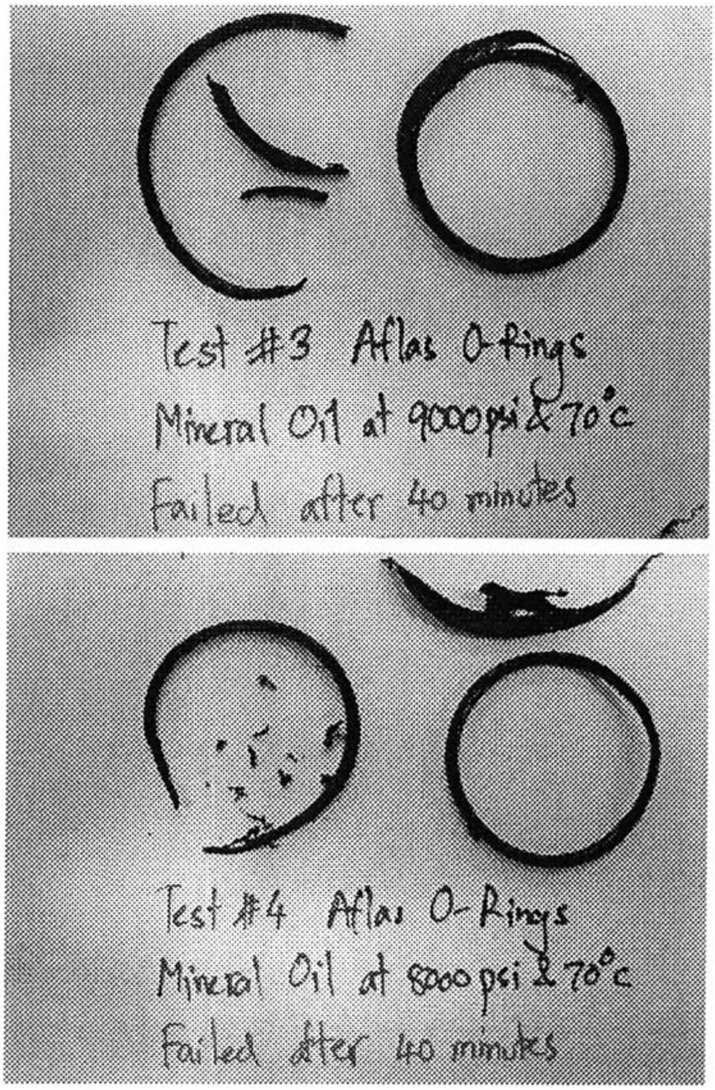

Figure B9 Aflas o-rings failed after 40 minutes

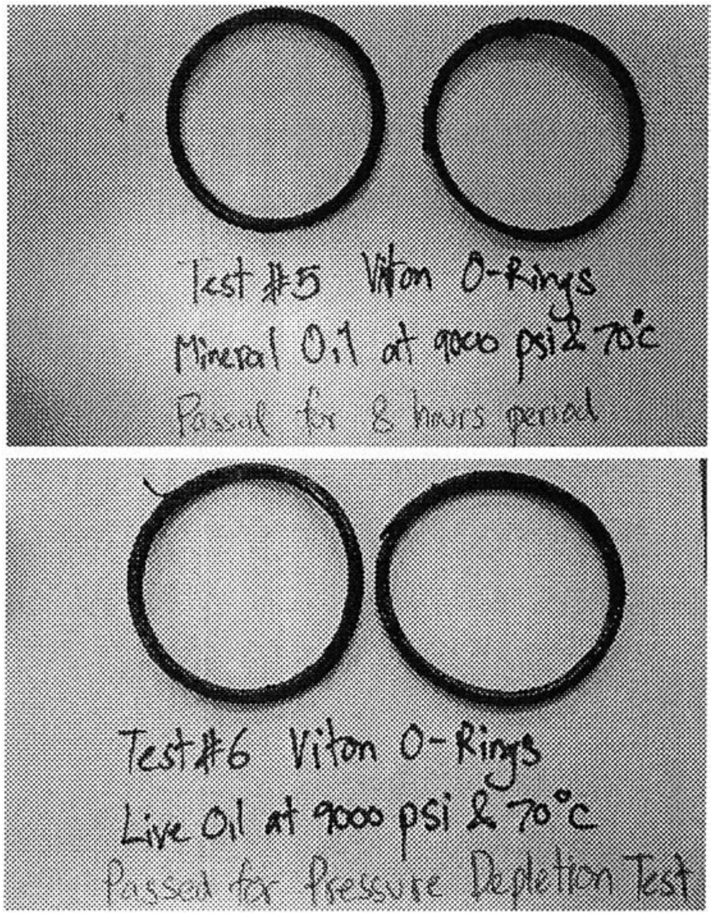

Figure B10 Viton o-rings passed the test

Appendix C Turbidity Measurement for Different Cases

Instead of the mean transmittance along the tube height, light transmittance can be represented at different tube heights (i.e., 25 % height, 50 % height, 75 % height, and 95 % height) as shown in Figure C1. The trend remains the same at any tube height that the light transmittance increased with time as asphaltene particles settled.

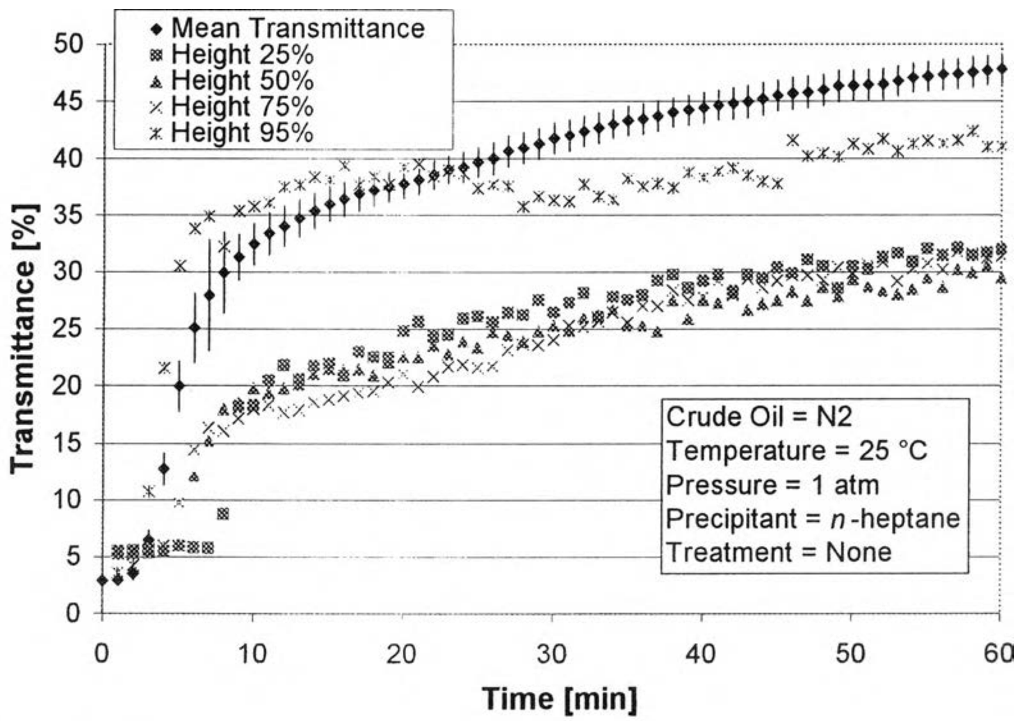

Figure C1 Transmittance at different tube heights

In the case that the residence time in the system is longer than 1 hour, one can perform this test with longer period to identify whether asphaltene precipitation will be a problem or not, as shown in Figure C2. The mean transmittance will increase until it reached equilibrium.

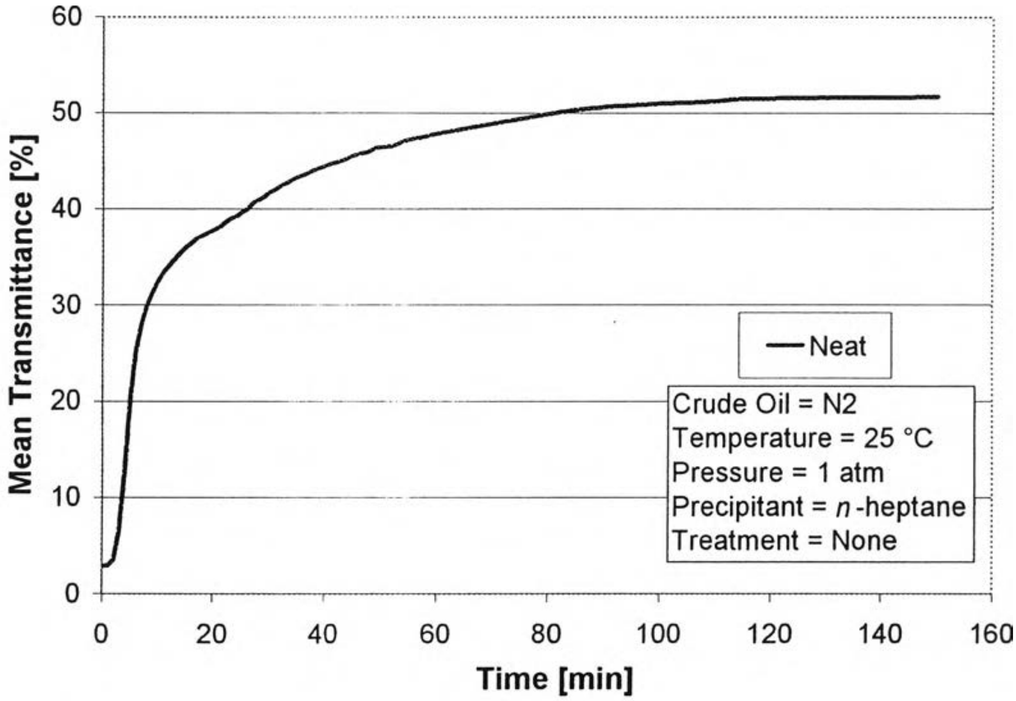

Figure C2 Transmittance for longer test

Asphaltenes settling can also be studied in different mediums with fixed solubility parameter to simulate different situations. The solubility parameter of the medium can be adjusted using mixture of toluene and *n*-heptane. The results are shown in Figure C3 that the higher the solubility parameter is, the lower the settling is (low light transmittance as asphaltenes still dispersed throughout the test tube.

Asphaltene settling can also be studied in different normal alkanes rather than *n*-heptane. The kinetic of precipitation and settling depends on the solubility parameter of normal alkanes and viscosity of those normal alkanes. The results in Figure C4 show that longer chain normal alkanes precipitated out and settled asphaltenes at a slower rate comparing to shorter chain normal alkanes.

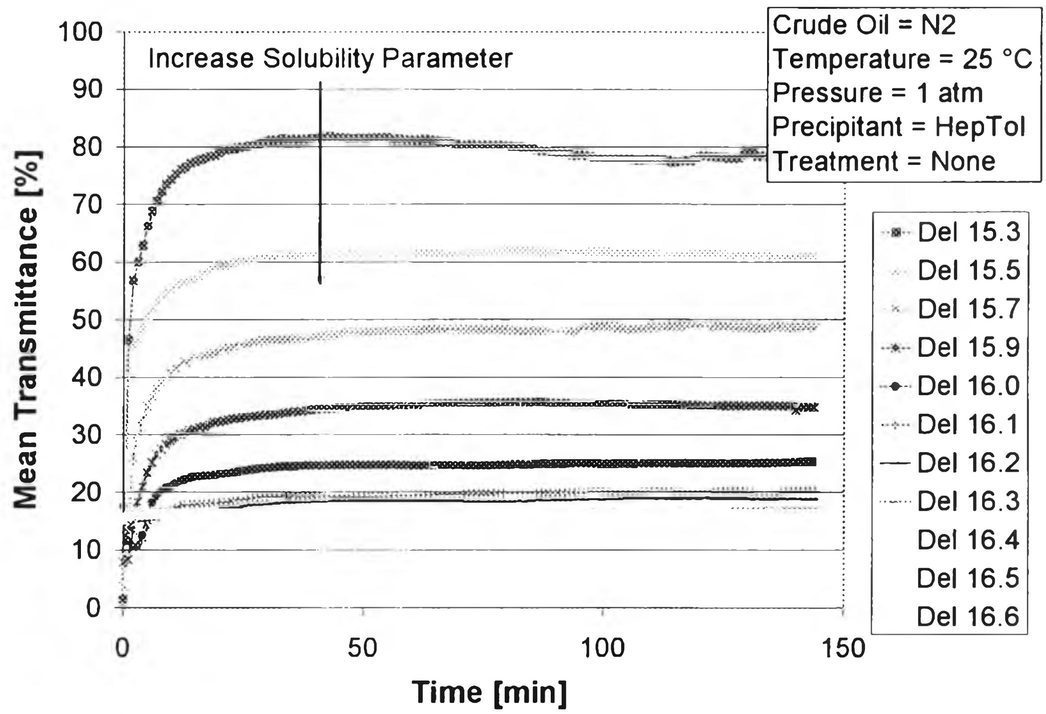

Figure C3 Mean transmittance with different solubility parameter mediums

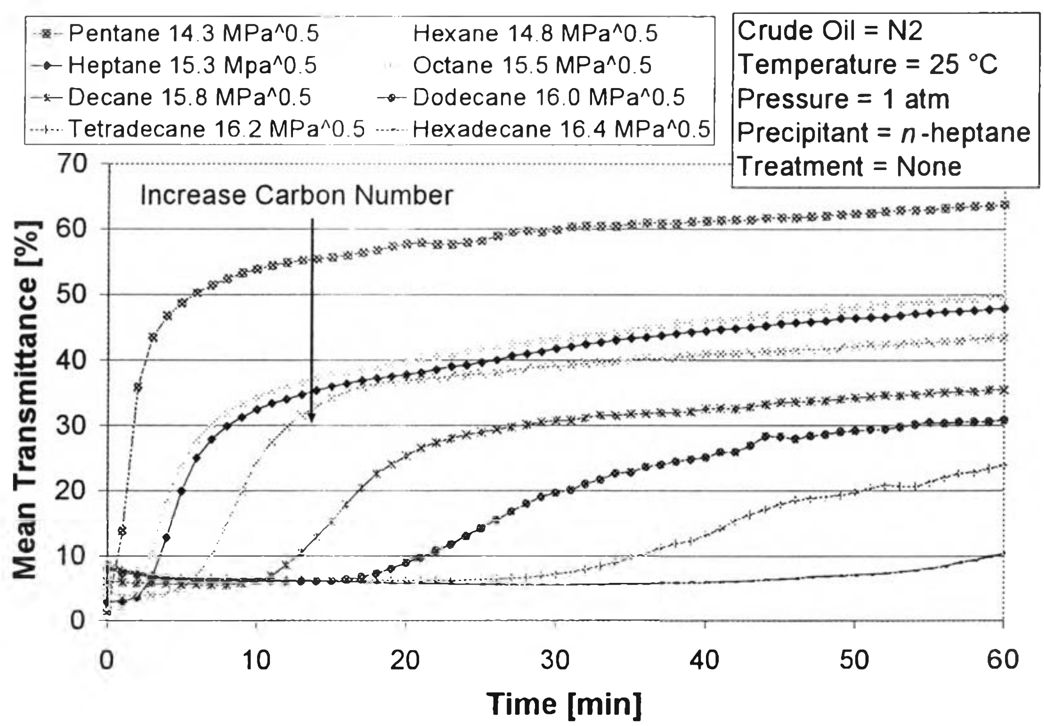

Figure C4 Mean transmittance with different normal alkanes

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2. Gharfeh, S., Singh, P., Kraiwattanawong, K., and Blumer, D. (2007) A general study of asphaltene flocculation prediction at field conditions. SPE Production and Operation, 22(3), 277-284.
3. Senra, M., Panacharoensawad, E., Kraiwattanawong, K., Singh, P., and Fogler, H. S. (2008) The role of *n*-Alkane polydispersity on the crystallization of *n*-Alkanes. Energy & Fuels, 22(1), 545-555.
4. Kraiwattanawong, K., Fogler, H. S., Gharfeh, S. G., Singh, P., and Chavadej, S. (2008) Mechanisms to control asphaltenes in unstable crude oil systems. (In review).

Presentations:

1. Kraiwattanawong, K., Fogler, H. S., Gharfeh, S. G., Singh, P., Thomason, W. H., and Chavadej, S. (2006, June 25-29) Thermodynamic solubility model to predict asphaltene instability in live crude oil. Paper presented at The 7th International Conference on Petroleum Phase Behavior and Fouling, Asheville, North Carolina, U.S.A.

2. Kraiwattanawong, K. and H. Scott Fogler (2006, October 3-5) Future asphaltene research with implication on oil and gas production flow assurance. Presented at Eureka Workshop: Flow Assurance SIG – Inorganic Scales and Organic Deposits, Edmonton, Canada.
3. Kraiwattanawong, K., Fogler, H. S., Gharfeh, S. G., Singh, P., Thomason, W. H., and Chavadej, S. (2006, November 12-17) Thermodynamic validation of asphaltene phase transition phenomenon using high pressure NIR cell. Presented at the AIChE Annual Meeting 2006, San Francisco, California, U.S.A.
4. Kraiwattanawong, K., Fogler, H. S., Gharfeh, S. G., Singh, P., and Chavadej, S. (2007, June 10-14) Mechanisms to control asphaltenes in unstable systems. Paper presented at The 8th International Conference on Petroleum Phase Behavior and Fouling, Pau, France.
5. Kraiwattanawong, K., Fogler, H. S., Gharfeh, S. G., Singh, P., and Chavadej, S. (2007, June 25-28) Mechanisms to control asphaltenes in unstable systems. Paper presented at The 2nd International Conference on Advances in Petrochemicals and Polymers, Bangkok, Thailand.