



## CHAPTER V

### CONCLUSIONS AND FUTURE WORK

#### 5.1 Conclusions

The ambient titrations were performed at different temperatures (25 °C, 45 °C, and 60 °C) with different normal alkanes (*n*-pentane, *n*-heptane, *n*-octane, *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane) for calculations of the solubility parameter of crude oil and the onset solubility parameter with different normal alkanes. The onset solubility parameters were plotted with different parameters (i.e., the carbon number of the precipitant, the molecular weight of the precipitant, the molar volume of the precipitant, the square root of the molar volume of the precipitant, the molar volume of the mixture, and the square root of the molar volume of the mixture) and all gave a very good linear fit with an  $R^2$  value greater than 0.995. However, the extrapolation of linear fit with different parameters for methane, ethane, propane and *n*-butane are not the same. Therefore, the extrapolation was validated using newly constructed high pressure system with laser near-infrared detector.

High pressure titrations were performed at 1000 psig and 25 °C where ethane, propane and *n*-butane were in liquid phase. The amount of precipitant required to initiate asphaltene precipitation for ethane is lower than propane and substantially lower than *n*-butane as expected. The high pressure titration results showed that the onset solubility parameter obeyed the partial Gibbs free energy of mixing as proposed by Hirschberg *et al.* in 1984 and also followed the linear extrapolation with the square root of the molar volume of the mixture. High pressure titrations at elevated temperatures (70 °C) with all normal alkanes from ethane to *n*-hexadecane were also performed. The onset solubility parameters were plotted with the square root of the molar volume of the mixture and showed a linear fit. Therefore, this correlation was used for all predictions.

The model prediction consisted of two parts; the live oil solubility parameter calculation and the onset solubility parameter prediction. The live oil solubility parameter was calculated from the solubility parameter of stock tank oil and the

solubility parameter and dissolved gases. The onset solubility parameter was predicted using the correlation between the onset solubility parameter and the square root of the molar volume of the mixture. The model prediction showed that the live oil was stable by itself and created no asphaltene precipitation. Miscible injectant (separator gases) was added to the model prediction. At 50 mol % miscible injectant, the model prediction showed that a bubble point pressure was at 5192.5 psia and the asphaltene precipitation onset pressure was at 7500 psia.

The pressure depletion experiment was performed to validate the model prediction. The stock tank oil was recombined with separator gases to generate the recombined live oil. Then, the recombined live oil was blended with miscible injectant at 50:50 molar ratios. The pressure depletion experiment was performed from 9000 psig to 3000 psig at a rate of decreasing of 20 psi per minute. The pressure depletion experimental result showed the bubble point pressure of 5175 psia and the asphaltene precipitation onset pressure of 7765 psia. The bubble point pressure and the asphaltene precipitation onset pressure were in good agreement with the model prediction and confirmed the model prediction. Therefore, this model prediction can be used to predict the asphaltene precipitation onset pressure for other combinations.

In the case that asphaltene precipitation could not be avoided, asphaltene chemicals (asphaltene dispersants) can be used to stabilize small asphaltene aggregates and prevent them from settling. Asphaltene chemicals were studied with different experimental techniques; automatic titration, optical microscope, turbidity measurement, and particle size distribution measurement. The automatic titration of crude oil with different asphaltene chemicals showed the delay of asphaltene precipitation onset because asphaltene chemicals stabilized asphaltene in smaller aggregates and this was confirmed by optical microscope. Next, the turbidity measurement was used to differentiate among ineffective chemicals, less effective chemical and more effective chemicals then ranked the effectiveness of these chemicals. The chemical screening scheme was also developed to help selecting the best chemical for particular crude oil which has a huge economic impact to oil industry. The particle size distribution was also performed for crude oil in different medium without asphaltene chemical. The results showed that asphaltenes in nature

are less than 0.1 micron called stable asphaltenes. When stabilized (either by resins or natural surfactants or chemical additives), they have the size range of 0.1 - 1 micron called colloidal asphaltenes. The asphaltene aggregates over 1 micron in diameter are called flocculated asphaltenes. The PSD results also showed that treating crude oil with a better chemical or more chemical concentration reduced the flocculated asphaltenes and increased the stabilized asphaltenes. As mentioned earlier, selecting the right chemical and concentration will reduce chemical treatment cost and make the project more profitable.

## 5.2 Future Work

There are a lot of researches on asphaltenes needed to be done to fully understand and to be able to tackle asphaltene issues. The followings are several suggestions on asphaltene research.

First, the effect of miscible injectant (light alkane gases) had been studied and our model prediction performed very well in predicting the asphaltene onset pressure. However, carbon dioxide flooding/injection to enhance oil recovery have been used extensively without the validation of model prediction. Therefore, the effect of carbon dioxide on the asphaltene precipitation of the live oil needs to be studied. This study can be performed with newly constructed high pressure system.

Second, the effects of asphaltene dispersants were studied under ambient conditions and successfully classified different types of asphaltene dispersants (i.e., ineffective, less effective and more effective chemicals). However, the effects of these chemicals under high pressure and high temperature have yet to be studied. Therefore, high pressure system can be used to study the effects of asphaltene dispersants under high pressure/high temperature conditions including downhole conditions.

Third, the effects of asphaltene dispersants were studied for a specific period of time. The kinetic study of asphaltene precipitation with or without asphaltene dispersants have yet to be studied. Turbiscan can be used to study the kinetic of asphaltene precipitation and settling with proper dispersing medium.

Fourth, the particle size distribution measurements were studied in very extreme environment (total precipitation) and lacked of the kinetic effect. Therefore, the particle size distribution change as a function of time needed to be studied. Asphaltene dispersants can also be studied with particle size distribution to see the effect of these chemicals on PSD.

Finally, the particle size distribution change as a function of time can be modeled using kinetic constants that can be obtained from the experiment.