CHAPTER IV
RESULTS AND DISCUSSION

4.1 Effects of Soluble Asphaltenes on Aggregation Kinetics

Soluble asphaltenes was fractionated from BR and GM asphaltenes by the method described in section 3.4.6. For GM asphaltenes, the concentration of solution used was 6.3 wt% asphaltenes, 56.7 wt% toluene and 37 wt% n-heptane. For BR asphaltenes, the concentration of solution used was 1.8 wt% asphaltenes, 58.2 wt% toluene and 40 wt% n-heptane. At this concentration, the detection time of both asphaltenes is approximately 12 hours and the insoluble asphaltenes accounted for 20 wt% of the total asphaltenes.

To investigate the effect of soluble asphaltenes, the soluble asphaltenes were mixed with insoluble asphaltenes at different proportions and prepared model oils with toluene. N-heptane was then added to the model oils. The content of the solution obtained was kept the same as the content at which the asphaltenes were fractionated to eliminate the effects of n-heptane and asphaltenes concentration. The solution obtained was examined with microscopy technique described in section 3.4.5. Detection time results for BR model oils are shown in Figure 4.1.
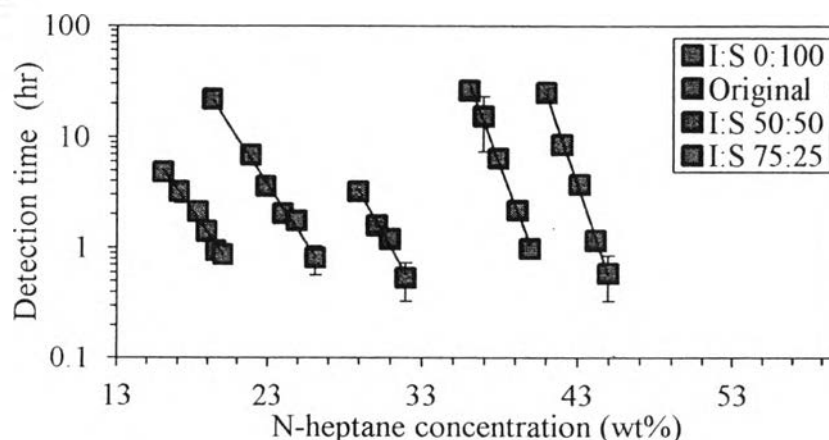

Figure 4.1 Detection as a function of n-heptane concentration at different BR soluble/insoluble ratio for BR model oils. All experiments were conducted at room temperature.

From Figure 4.1, as the curve shifts to the right, the asphaltenes are more stable because it need more time to be detected under microscope at same n-heptane concentration. The curves shift to the right as the soluble/insoluble ratio increases. To emphasize the effect, the detection time was plotted against soluble/insoluble ratio, as shown in Figure 4.2. As the ratio increase, the detection time increase, indicating the increase in stability of insoluble asphaltenes. The same trends were observed in GM asphaltenes as shown in Figure 4.3.
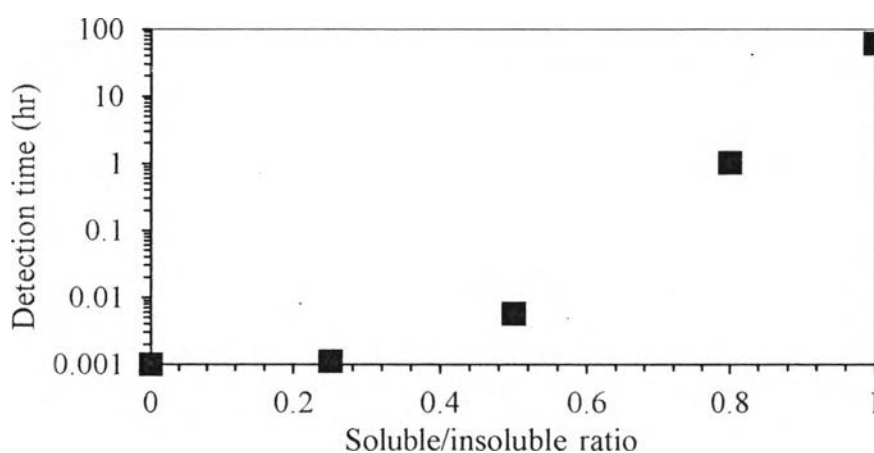
Figure 4.2 Detection as a function of n-heptane concentration at different BR soluble/insoluble ratio.
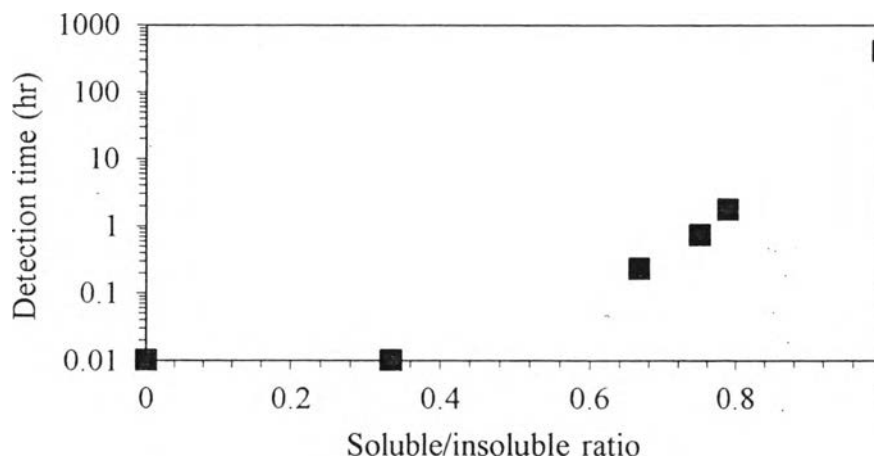
Figure 4.3 Detection as a function of n-heptane concentration at different GM soluble/insoluble ratio.

The experimental results in Figure 4.1-4.4 show that the soluble asphaltenes alter the aggregation kinetics of insoluble asphaltenes. The presence of soluble asphaltenes increases the detection time of aggregation, or in other word, delays the aggregation process. There are four possible mechanisms that might be the reason behind this phenomena. First, the increase in soluble content contributes to the increase in viscosity, which consequently reduces the collision frequency and thus decrease the number of successive collisions. Second, the increase in soluble content contributes to the decrease in diffusivity due to the molecular barrier, which also results in the decrease the number of successive collisions. However, these two possibilities were disproved by the calculation using numbers of experimental data. The calculation for the viscosity and diffusivity is included in Appendix B.

The third possible explanation is that the soluble asphaltenes help solvate the insoluble, which is called "solvation" effects. In this effect, the soluble asphaltenes will adsorb on the surface of insoluble asphaltenes, acting like a protective layer. As the surface is covered by the protective layer, the number of successive collisions will decrease. The last possible explanation is the reverse of the third. The soluble asphaltenes do *not* solvate the insoluble directly, but increase the stability of the insoluble by being a *part* of the solution, making the solution to be more hospitality for the insoluble. This explanation was implicitly proposed by Haji-Akbari *et al.* (2014) as they use their unified aggregation model to explain numerically how the oils having more asphaltene content are more stable than the lower one. They had used "solubility parameter (δ)", which is defined as the square root of ratio between vaporization energy and molar volume, to assess the hospitality of the solution for the insoluble asphaltenes. As the solubility parameter of solution medium and insoluble asphaltenes become closer, they will be more compatible. The soluble asphaltenes will decrease the difference between solubility parameter of solution medium and insoluble asphaltenes. However, they have no experimental evidences of how the soluble asphaltenes be a true part of solution. Furthermore, this will contradict with the belief that the asphaltenes exist in colloidal form in both model and crude oils. The third and fourth hypothesis can be proved experimentally by SAXS method, which will be discussed in section 4.3.

4.2 Effects of Soluble Asphaltenes on Equilibrium Solubility

BR asphaltenes was used to extract soluble and insoluble asphaltenes by the method described in 3.4.6. The mixture content was 1.2 wt% asphaltenes, 38.8 wt% toluene and 60 wt% n-heptane. The BR soluble, insoluble and 50:50 mixtures of them were then mixed with toluene to make model oils. The n-heptane was then added to the model oils. The mixture content was kept the same as the content at which the soluble and insoluble was extracted. The mixture was then underwent centrifugation experiment described in 3.4.7 to obtain solubility of asphaltenes as a function of time, which as shown in Figure 4.4.
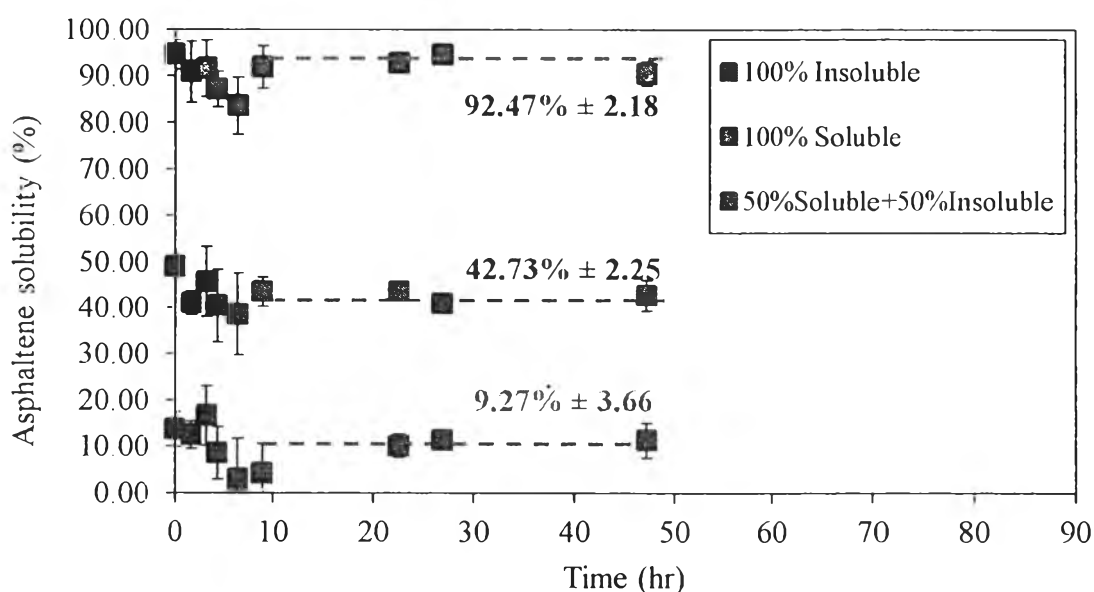

Figure 4.4 Asphaltene solubility as a function of time for soluble, insoluble and 50:50 sol/insol asphaltenes. After 20 hours, the solubility become constant with time and the equilibrium solubility was obtained, indicated by dash lines.

The asphaltene solubility in this study is defined as the weight percent of the dried cake per the total mass of asphaltenes in solution taken to centrifuge. As the time increase, the solubility usually becomes lower until reach a plateau, where the solubility at equilibrium or equilibrium solubility can be obtained. In this experiment, the concentration of n-heptane was very high, so that we could not clearly see the decrease

in solubility over time. However, the equilibrium solubility still can be seen after 20 hours.

The equilibrium solubility of soluble and insoluble asphaltenes was 92.47 and 9.27 wt%, respectively. The values obtained is out of expectation, because this experiment was performed under the same solution content that the soluble and insoluble asphaltenes were extracted. So, the solubility of soluble and insoluble should be 100 and 0%, respectively. This could be because of the cross-contamination between the soluble and insoluble during extraction process, as the solubility of the soluble become lower and the solubility of insoluble become higher. The 50:50 sol/insol sample will be affected by this error because the actual ratio might not be 50:50. However, the error was accounted by treating the excess solubility of the insoluble as the soluble and vice versa. To illustrate, the insoluble asphaltenes in this experiment had been treated as a solid mixture of 9.27% soluble asphaltenes and the rest is the insoluble asphaltenes. Similary, the soluble asphaltenes had been treated as a solid mixture of 92.47% soluble asphaltenes and the rest will be the insoluble. After doing mass balance calculation, the actual ratio of 50:50 sol/insol sample is 49.13:50.87, which is close enough to the expected concentration.

The equilibrium solubility obtained from the 50:50 sol/insol sample can be used to determine whether the soluble asphaltenes affect the equilibrium solubility. If the soluble asphaltenes have no effect on the equilibrium solubility, the equilibrium solubility obtained for this sample should be 49.13%, as all of the insoluble should be separated out. However, from Figure 4.4, it can be seen that the equilibrium solubility is 42.73% ± 2.25, which means that 42.73% of the total asphaltenes in mixture or 7.27% of soluble asphaltenes were aggregated and separated out. In other word, some of the soluble asphaltenes becomes insoluble. However, this is mainly due to the method of centrifugation, as the soluble asphaltenes could be trapped in the cake, increasing the yield of asphaltenes precipitated. However, it is still safe to say that the soluble asphaltenes do *not* alter the equilibrium solubility of the insoluble, as all of the insoluble asphaltenes remain *insoluble*.

4.3 Molecular Nature of Soluble and Insoluble Asphaltenes Studied by SAXS

As briefly described in 4.1, the third hypothesis, which is the solvation effect by the soluble, and fourth hypothesis, which is the solution improvement effect by the soluble, could be tested by SAXS method. SAXS, or small-angle X-ray scattering is a method that can be used to gain data in molecular level, such as size, fractal dimension along with the interaction between the molecules.

The molecular schematic of third and fourth hypothesis is shown in Figure 4.5a and 4.5b, respectively. In Figure 4.5a, the soluble asphaltenes adsorb on the surface of the insoluble, acting like a barrier for collision, resulting in decrease in collision efficiency. Adversely, in Figure 4.5b, the soluble do not adsorb on the surface of the insoluble. These two hypotheses can be distinguished by the scattering intensity profile. If there is no solvating effect, by super-position principle, the scattering of mixture must be the summation of scattering of each component in the mixture. Conversely, if there is solvating effect, the scattering of solvating component will overlapped the other and thus the scattering of mixture will not equal to the summation of each component.
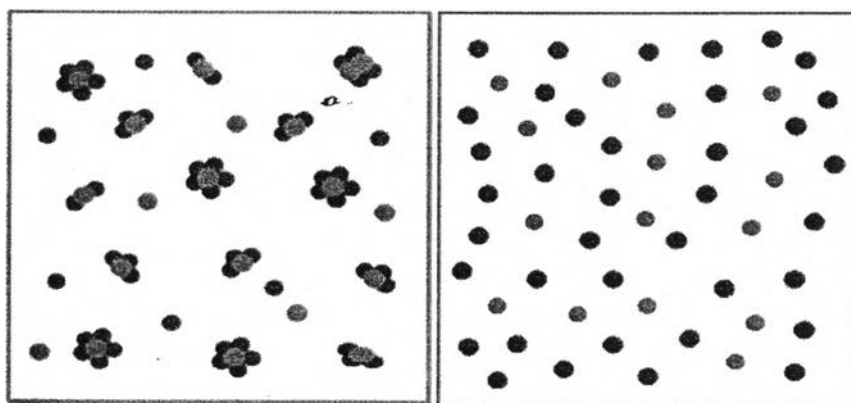

Figure 4.5 Schematic of insoluble and soluble asphaltenes in molecular level. In the left figure, soluble asphaltenes "solvate" the insoluble. In the right figure, the soluble do not solvate the insoluble.

The same soluble, insoluble and original GM asphaltenes used in 4.1 was used in this experiment. The model oil of 8, 2, 10 wt% of soluble, insoluble and original asphaltenes in toluene were made by method 3.4.3 and examined by SAXS. Figure 4.6 shows the intensity of X-ray scattered (I(q)) as a function of scattering vector (q) for soluble, insoluble and original model oil. The intensity shown here is the intensity normalized by volume fraction of toluene in the solution.
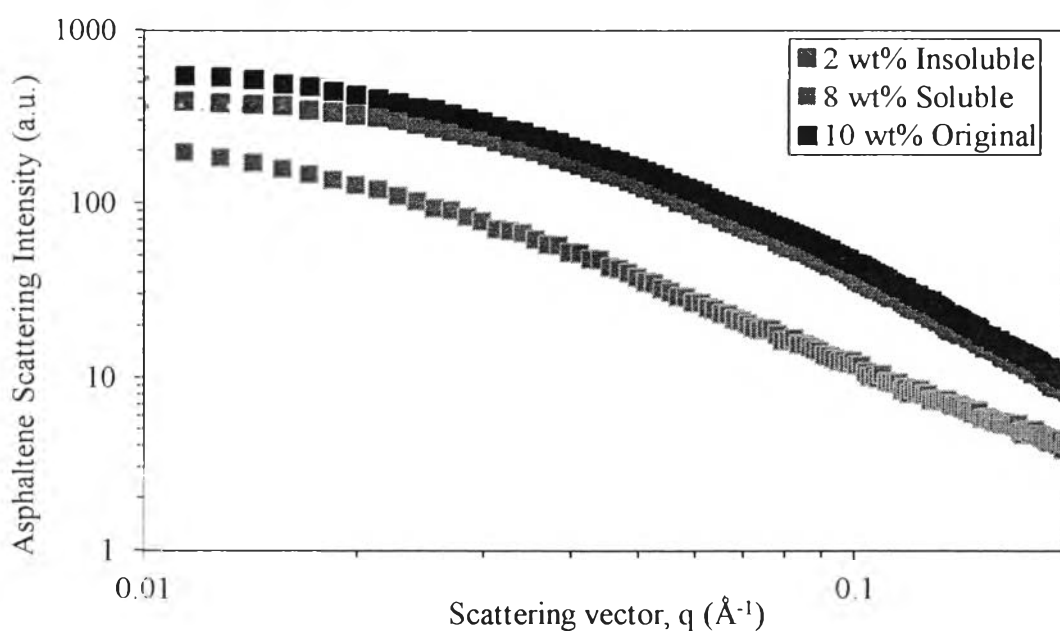

Figure 4.6 Scattering profile of 2wt% insoluble, 8 wt% soluble and 10 wt% original asphaltenes. The measurements were conducted at room temperature.

Due to the fact that +mass fraction of soluble and insoluble in original asphaltenes is 0.8 and 0.2, respectively. So, 10 wt% of original asphaltenes is basically a mixture between 8 and 2 wt% of soluble and insoluble. If there is no solvation, the scattering profile of 10 wt% original asphaltenes must be equal to summation of scattering profile of soluble and in soluble asphaltenes. The result of summation of soluble and insoluble compared to original asphaltenes is shown in Figure 4.7.
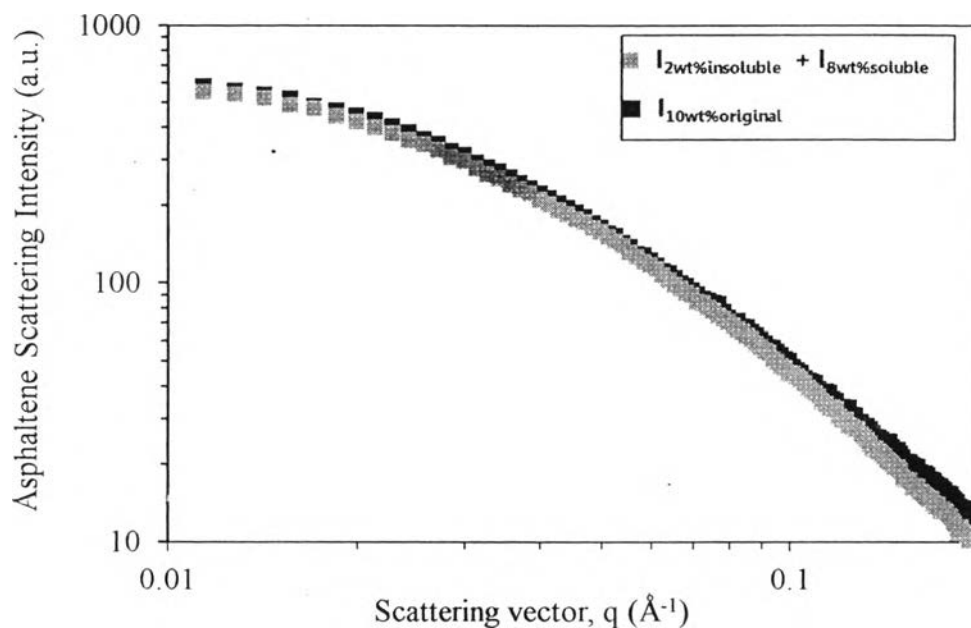
Figure 4.7 Comparison between I(q) of 10wt% original asphaltenes and summation of I(q) of 8wt% soluble and 2 wt% insoluble asphaltene model mixture.

It is clear that the intensity of 10 wt% original asphaltenes is statistically equal to the summation of intensity from insoluble and soluble asphaltenes. Thus, the soluble do not solvate the insoluble, but instead they are *part* of solution. This is an experimental evidence showing that the hypothesis proposed by Haji-Akbari *et al.* (2014) is true. The soluble asphaltenes help decrease the difference between solubility parameter of solution medium and insoluble asphaltenes, and thus increase the kinetical stability for the insoluble asphaltenes. According to the results from 4.1 and 4.2, it can be concluded that the soluble asphaltenes helps delay the aggregation process by increase the hospitality of the solution for the insoluble asphaltenes. So, kinetical stability of the insoluble is increased as the soluble content increase. However, after a certain period of time, All of the insoluble asphaltenes will eventually aggregate and separate out of the solution.

4.4 Effect of Oxygen from Air on Aggregation Kinetics and Equilibrium Solubility

To assess the effect of oxygen on aggregation kinetics and equilibrium solubility, two sets of experiment were prepared. First set was conducted in a glove chamber filled with nitrogen established using method 3.4.9-3.4.10. The second was performed in normal air environment. The crude oil used for the kinetics study is N2 crude oil and bitumen used in equilibrium soluility experiment is WC Bitumen.

Figure 4.8 shows the detection time of asphaltenes in N2 crude oil as a function of heptane concentration in nitrogen and air. From the figure, it can be seen that the detection time collected under nitrogen and air is overlapped and slight different at low and high n-heptane content, respectively. These results suggest that the oxygen has a negligible influence on asphaltene aggregation kinetics that could be noticed at low heptane concentration only, where the influence of n-heptane is suppressed.
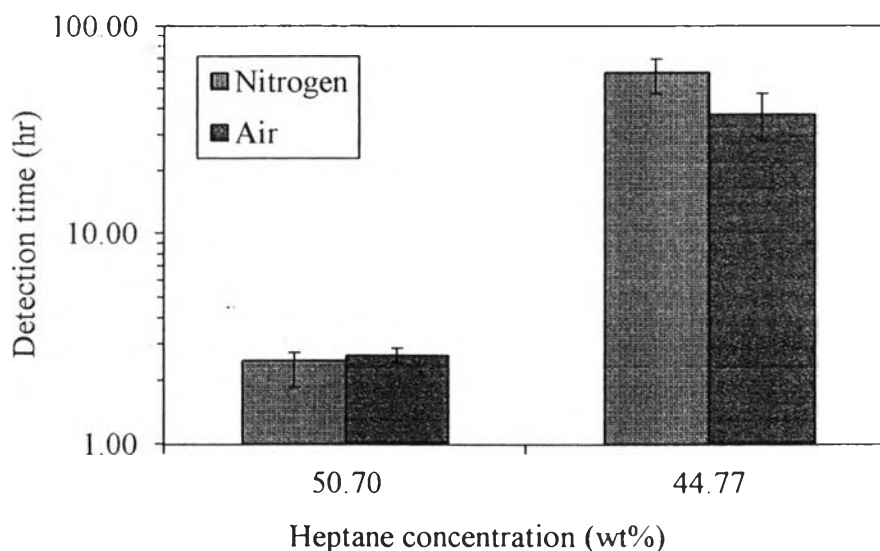

Figure 4.8 Detection time of asphaltenes in N2 crude oil under nitrogen and air environment. The experiment was conducted at room temperature.

Figure 4.9 shows the asphaltene solubility, represented by the asphaltene yields from centrifugation, as a function of time. The heptane concentration was kept at 64.5 wt%. It can be seen that the presence of oxygen cause an increase in asphaltene yields at longer time. However, similar to the kinetics, this increase is small compared

to the effect of heptane and can be neglected. The results also show that the degassing does alter the stability of asphaltene in WC bitumen but not significantly.
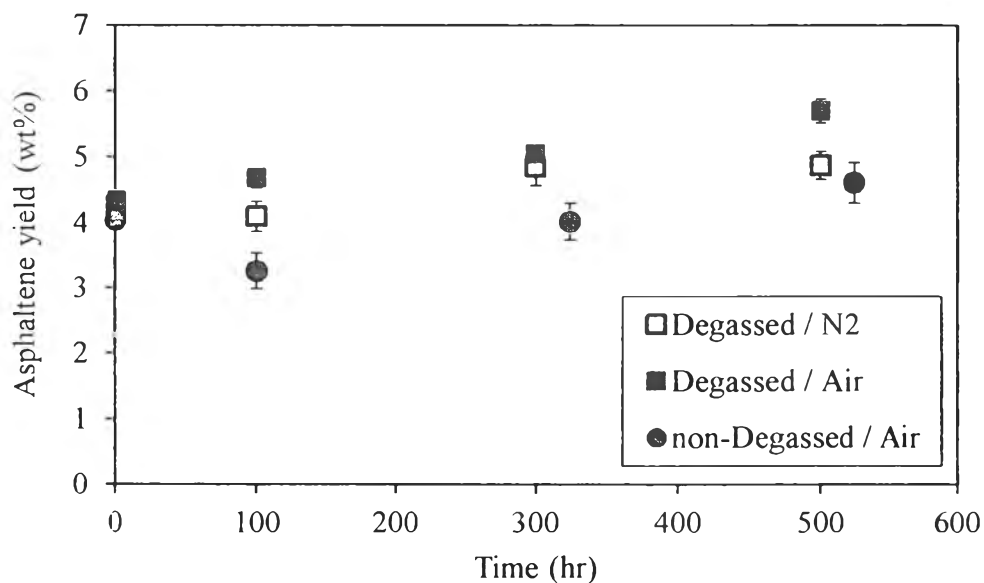

Figure 4.9 Asphaltene yield of WC bitumen as a function of time at different environments. All experiments were conducted at room temperature.

From Figure 4.8 and 4.9, it can be seen that the oxygen from air does affect the asphaltene aggregation in both kinetics and thermodynamics aspect. However, their effects is so small that can be negligible. The main factors that force the asphaltenes to aggregate in this study still be the effect of n-heptane. It can be seen that the effect of oxygen from air could be noticed only at low n-heptane concentration.

This results validate the experiment conducted under air environment, as the effect of oxygen from air is negligible, so the effect they observed was not been dominated by the effect of oxygen.

However, a drawback of this experimental setup is that the bitumen or crude oil used were exposed to air for long time before degassed and used. The oxygen from air might does some effects on the crude or bitumen for long time, so that the effect can not be observed in this relatively short-time experiment.