

CHAPTER IV

RESULTS AND DISCUSSION

As be described earlier in Chapter III, the original asphaltene was the insoluble fraction of the mixture between Zuata crude oil and heptane. Asphaltene yield obtained from Zuata crude was approximately 97 g/L.

The original Zuata asphaltene was aged in air at 90, 120, 150 and 180° C and under nitrogen environment at 60, 90,120 and 150 °C. Aging pressure was controlled constant at 25 in Hg vacuum.

The experimental studies were divided into three main parts of dissolution study, acid/base determination and asphaltene characterization. All experimental data from dissolution study were given in Appendix B.

4.1 Determination of Asphaltene Dissolution Kinetics

4.1.1 Effects of Aging Time on Asphaltene Dissolution

Each asphaltene sample which was aged at 120 °C for 1, 3, 5 and 7 days under either air or nitrogen environment was packed in the differential reactor in order to study the kinetics of asphaltene dissolution. Figures 4.1 and 4.2 show the dissolution profiles of 5 asphaltene samples aged at 120 °C, 25 in Hg vacuum and different aging times under nitrogen and air environment, respectively. The results showed that only unaged asphaltene could be completely dissolved with 10wt. % DBSA in heptane within a short period of time about 20 min. The degree of asphaltene dissolution decreased drastically with increasing aging time under both nitrogen and air environment due to an increase in molecular size and change in chemical structure, which will be explained in the next part.

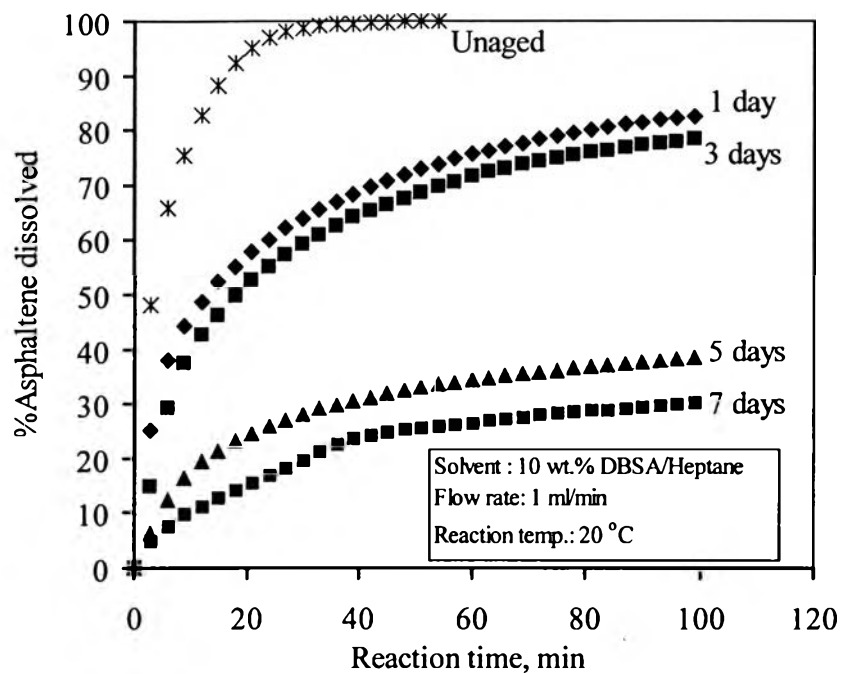


Figure 4.1 Dissolution profiles of asphaltenes aged at different aging times at 120 °C under nitrogen environment

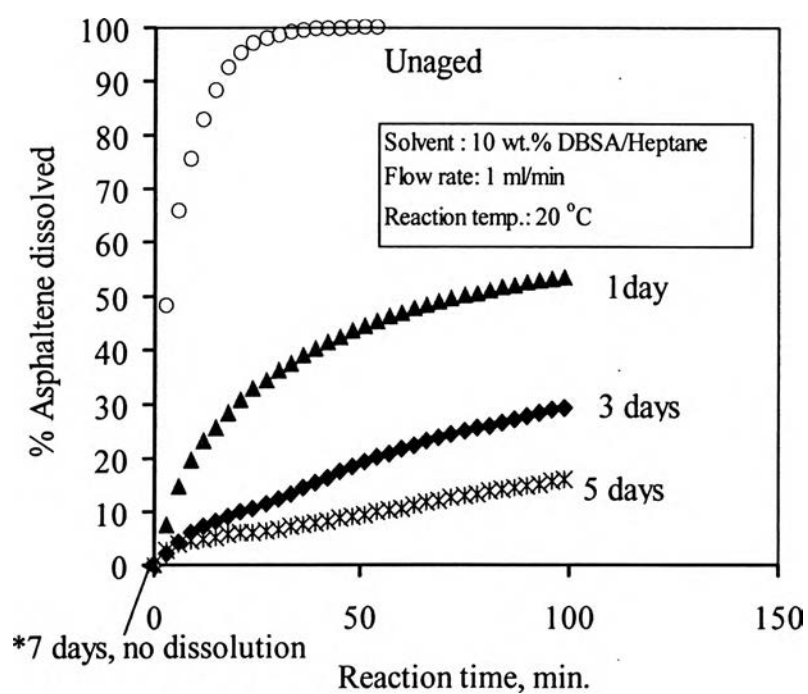


Figure 4.2 Dissolution profiles of asphaltenes aged at different aging times at 120 °C in air

Figures 4.3 and 4.4 show the effect of aging on the asphaltene dissolution by comparing the calculated values of the dissolution rate constants of unaged and aged asphaltene samples at different aging times under nitrogen and air environment, respectively. The dissolution rate constants of both aged under nitrogen and air environment decreased substantially with increasing aging time.

4.1.2 Effects of Aging Temperature on Asphaltene Dissolution

It is also clearly seen from Figures 4.5 and 4.6 that when aging temperature increases, the percentage of asphaltene dissolved decreases significantly for both asphaltene aged under nitrogen and air environment. It is very interesting to point out that for the aging temperature range of 60-120° C, the dissolution profiles were almost the same but it increased drastically when aging temperature exceeded 120°C. As shown in Figures 4.7 and 4.8, the apparent rate constants of the first order reaction model can be calculated from the slope of these plots. The results showed that apparent rate constants of aged asphaltenes decreased significantly with an increase in aging temperature.

The values of rate constants, k , of asphaltenes aged under both nitrogen and air environment are replotted as shown in Figures 4.9 and 4.10. For an aging temperature of 120 °C, when aging time increased, the apparent rate constant of asphaltene aged in air decreased more rapidly than one aged under nitrogen. For aging time of 3 days, the rate constant of asphaltene aged under nitrogen changed slightly in the temperature ranging from 60 to 120 °C but the rate constant of asphaltene aged in air changed rapidly. The results indicate both aging time and aging temperature affecting the asphaltene dissolution significantly. More discussion will be given in the next section.

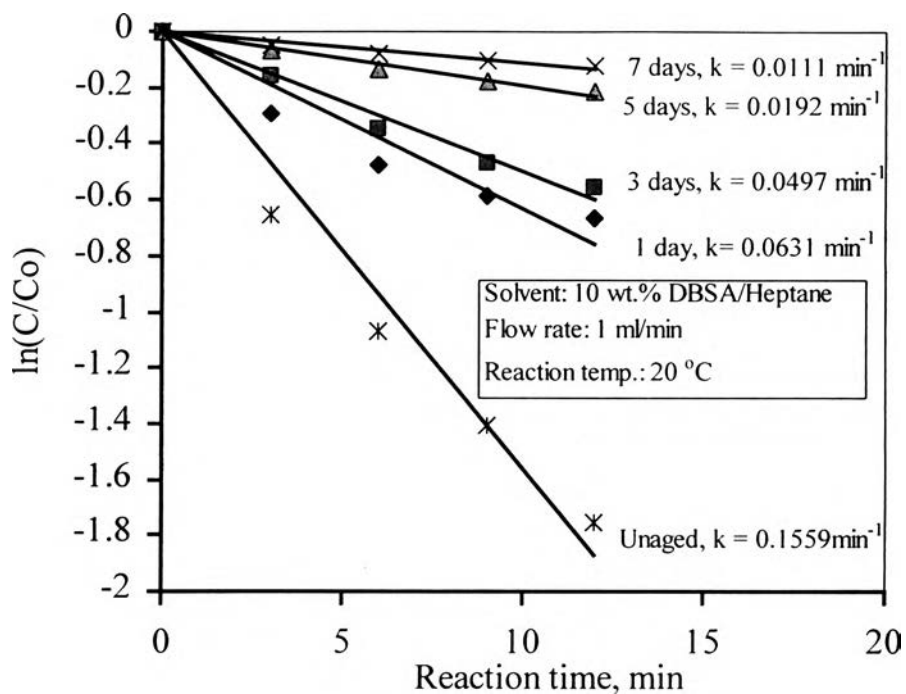


Figure 4.3 Kinetic analysis with first order reaction assumption when varying aging times under nitrogen environment at 120 °C

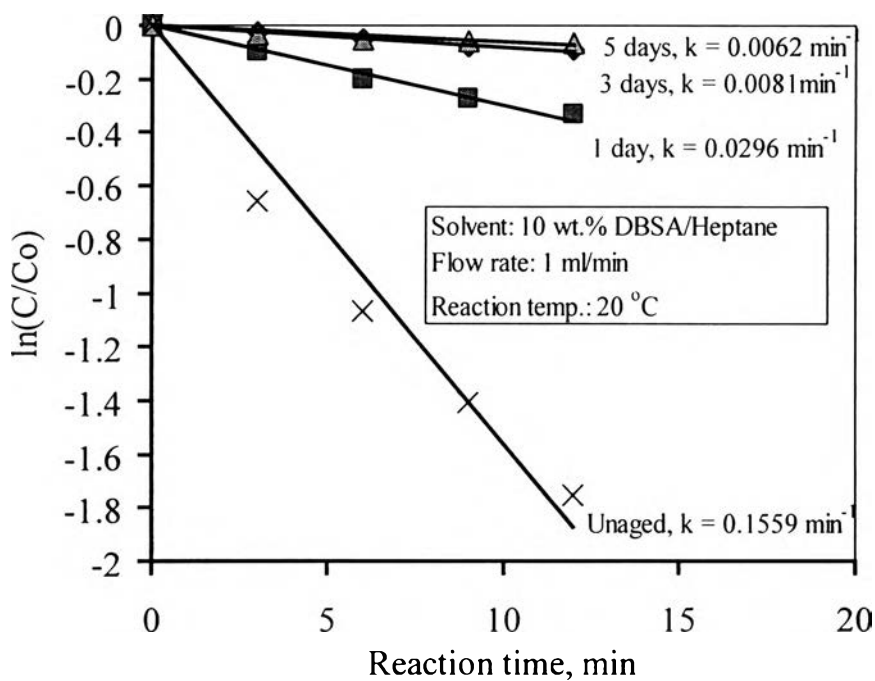


Figure 4.4 Kinetic analysis with first order reaction assumption when varying aging times in air at 120 °C

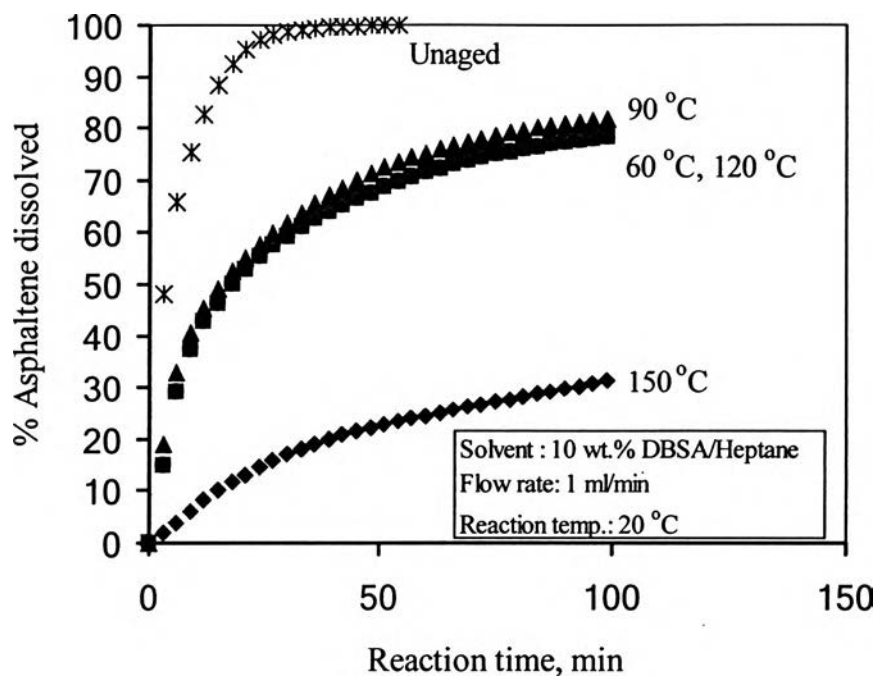


Figure 4.5 Dissolution profiles of asphaltenes aged at different aging temperatures when aged under nitrogen for 3 days

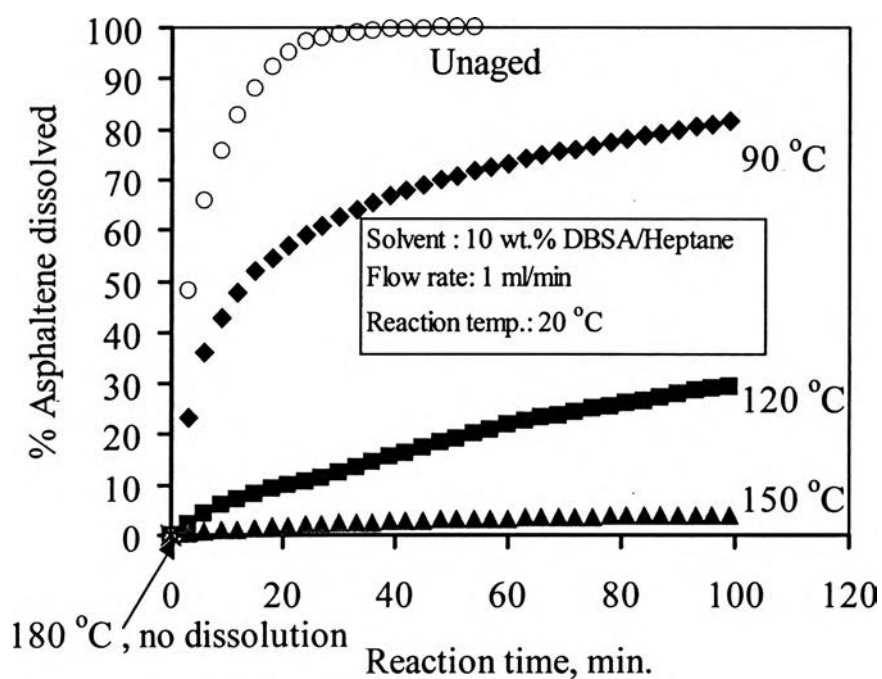


Figure 4.6 Dissolution profiles of asphaltenes aged at different aging temperatures when aged in air for 3 days

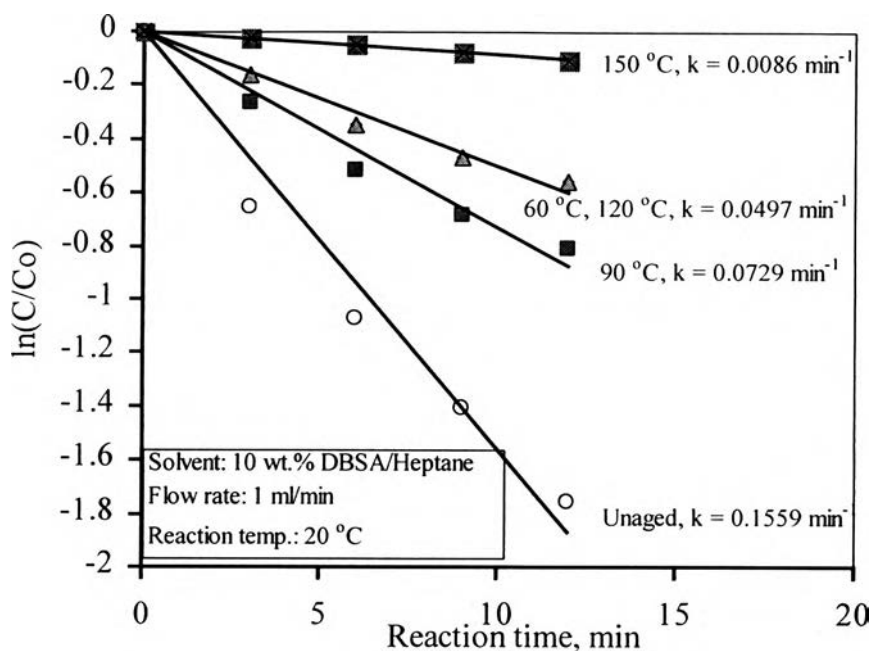


Figure 4.7 Kinetic analysis with first order reaction assumption to determine the dissolution rate constants of asphaltenes aged at different aging temperatures under nitrogen environment for 3 days

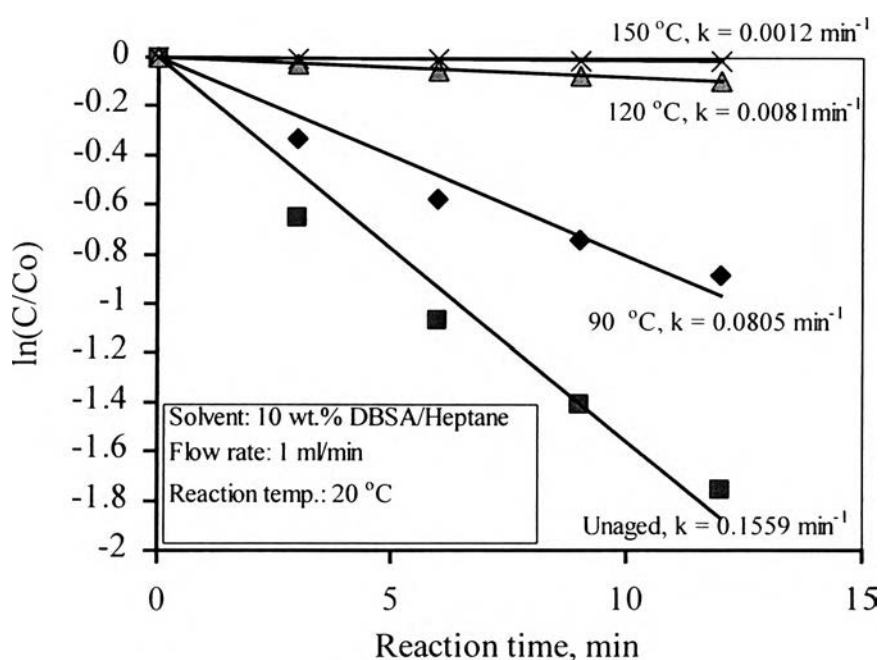


Figure 4.8 Kinetic analysis with first order reaction assumption to determine the dissolution rate constants of asphaltenes aged at different aging temperatures in air for 3 days

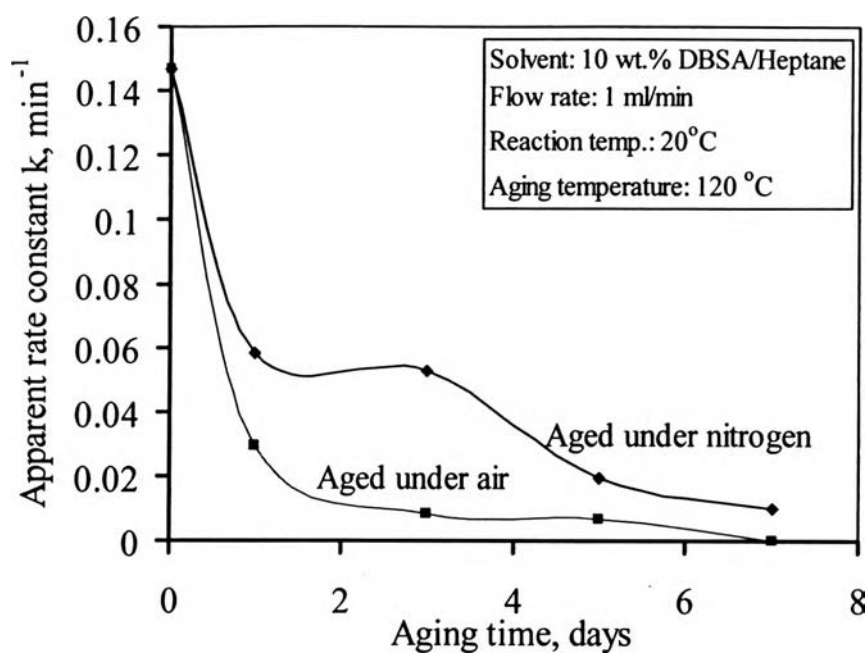


Figure 4.9 Apparent rate constant, k , as a function of aging time of asphaltene aged at 120°C under nitrogen and air environment

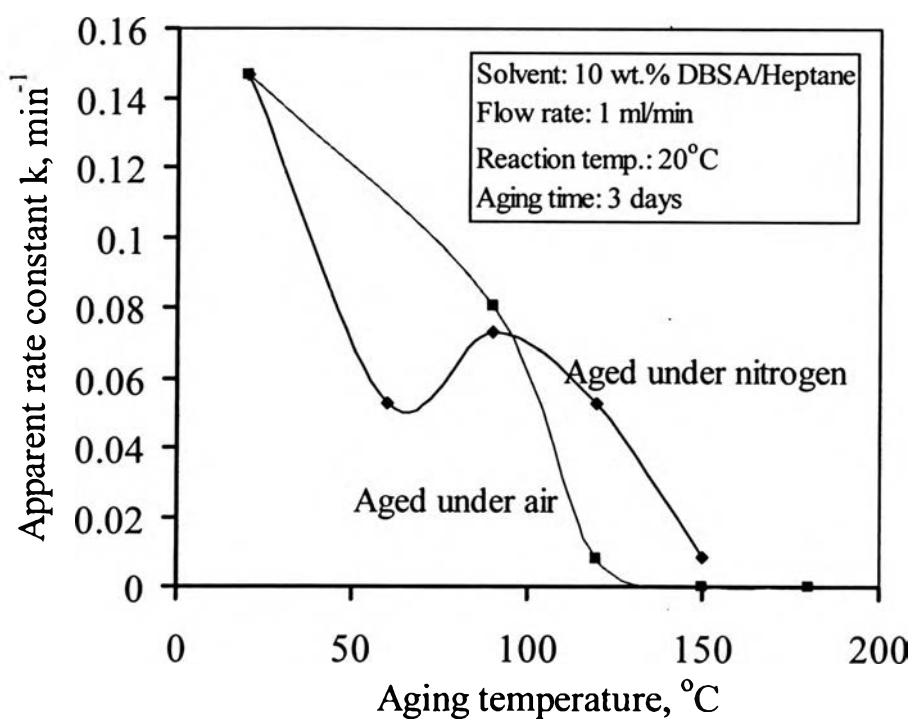


Figure 4.10 Apparent rate constant, k , as a function of aging temperature of asphaltene aged for 3 days under nitrogen and air environment

4.2 Acid and Base Properties of Aged Asphaltenes

The acid/base properties of asphaltenes can be demonstrated through the acid/base number. Acid/base number is the number of acid/base site equivalent to milligram of potassium hydroxide per gram sample. The titration curves obtained from potentiometric titration of asphaltene samples had one inflection point at about $E = 130$ to 160 mV for acid titration and $E = -160$ to -240 mV for base titration as shown in Appendix A.

4.2.1 Effects of Aging Temperature on Acid and Base Number

Acid/base numbers of aged asphaltenes were calculated and plotted as a function of aging temperature at constant aging time in order to determine the correlation between aging condition and acid/base number. From the results shown in Figure 4.11, for asphaltene aged under nitrogen environment at an aging time of 3 days, both acid and base numbers decrease with increasing aging temperature due to the condensation reactions. For the case of asphaltenes aged in air as shown in Figure 4.12, the change in acid/base numbers is different when compared to asphaltenes aged under nitrogen environment. Even though three samples aged at 120 °C and 7 days, 150 °C and 3 days, and 180 °C and 3 days were not completely dissolved in the titration solvent, the acid number seemed to decrease slightly from that of unaged to 90 °C aging temperature, then increased slightly when aging temperature increased to 120 °C. Beyond 120 °C, if aging temperature still increased, the acid number increased significantly. However, the base number decreased gradually with increasing aging temperature.

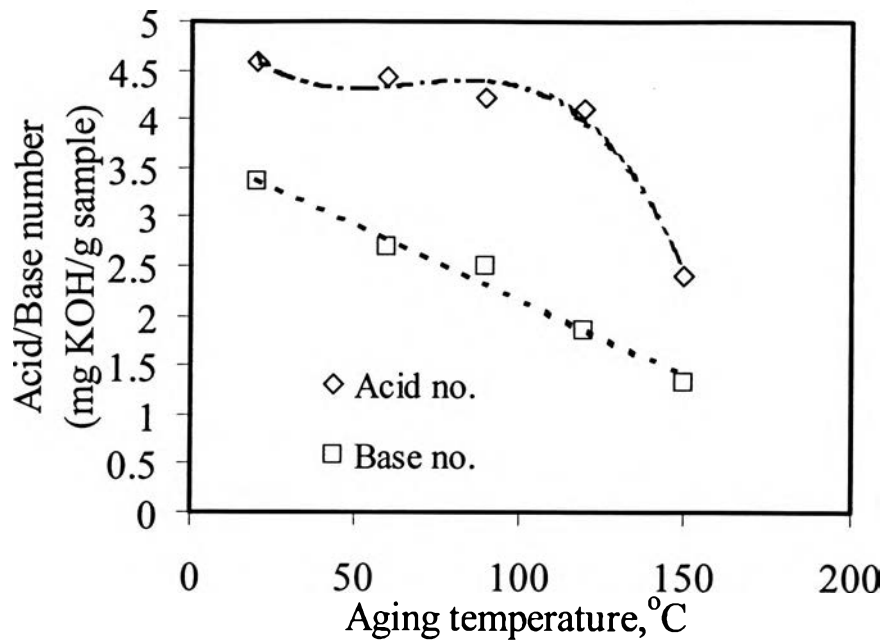


Figure 4.11 Relationship between acid/base number and aging temperature of asphaltene at constant aging time of 3 days under nitrogen environment

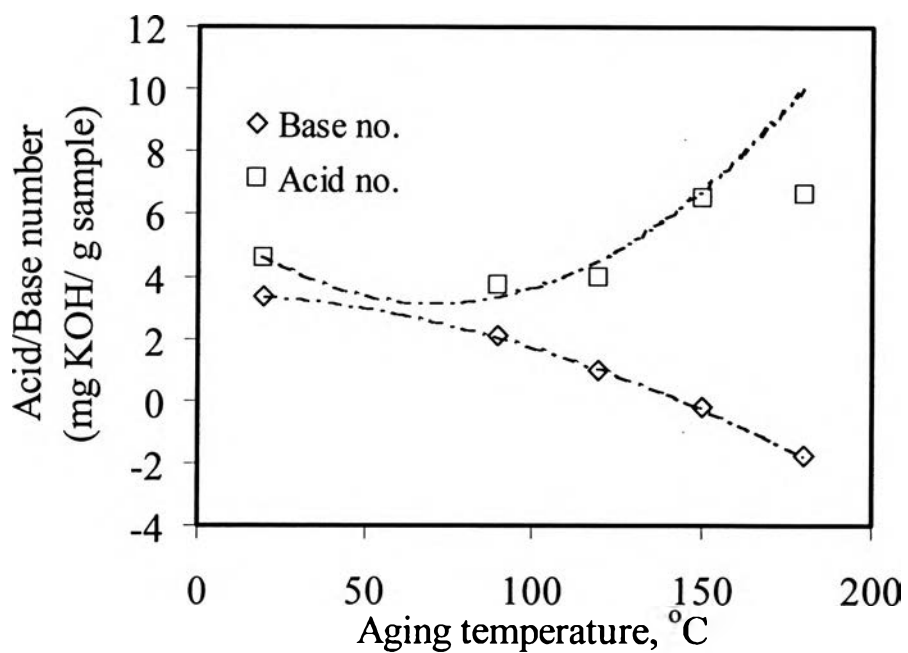


Figure 4.12 Relationship between acid/base number and aging temperature of asphaltene at constant aging time of 3 days in air

4.2.2 Effects of Aging Time on Acid/Base Number

Figures 4.13 and 4.14 show the relationship between aging time and acid/base number of asphaltene aged at 120 °C under nitrogen and air environment, respectively. As can be seen from Figure 4.13, the base number of asphaltene aged under nitrogen environment decreases substantially but the acid number decreased slightly with increasing aging time. These decreases in both acid and base numbers are probably due to condensation polymerizations. For asphaltene aged in air as shown in Figure 4.14, the acid number significantly increases but the base number seems to decrease slightly and level off with long period of aging process when the aging temperature increases. An increase in the acid number of asphaltene aged in air firmly confirms the occurrence of oxidation reaction.

4.3 Correlation between Acid/Base Number and Dissolution of Asphaltenes

The percentage of asphaltene dissolved and the apparent dissolution rate constant after contacting with 100 ml of 10 wt. % DBSA in heptane of each sample were calculated and replotted in order to determine the correlation between the acid/base number and the dissolution of asphaltenes. Figure 4.15 shows the good relationship between the percentage of asphaltene dissolved and the base number and Figure 4.16 shows the relationship between the apparent rate constant and the base number of asphaltene aged under different conditions. The percentage of asphaltene dissolved increased with increasing base number until it reached 100 % asphaltene dissolved at base number equal 3.37. This increase in the asphaltene dissolution is due to the interaction between asphaltene base site and DBSA acid site. The sulfonic group of DBSA tends to react with the base group in asphaltene affecting the increases in the dissolution and the apparent rate constant.

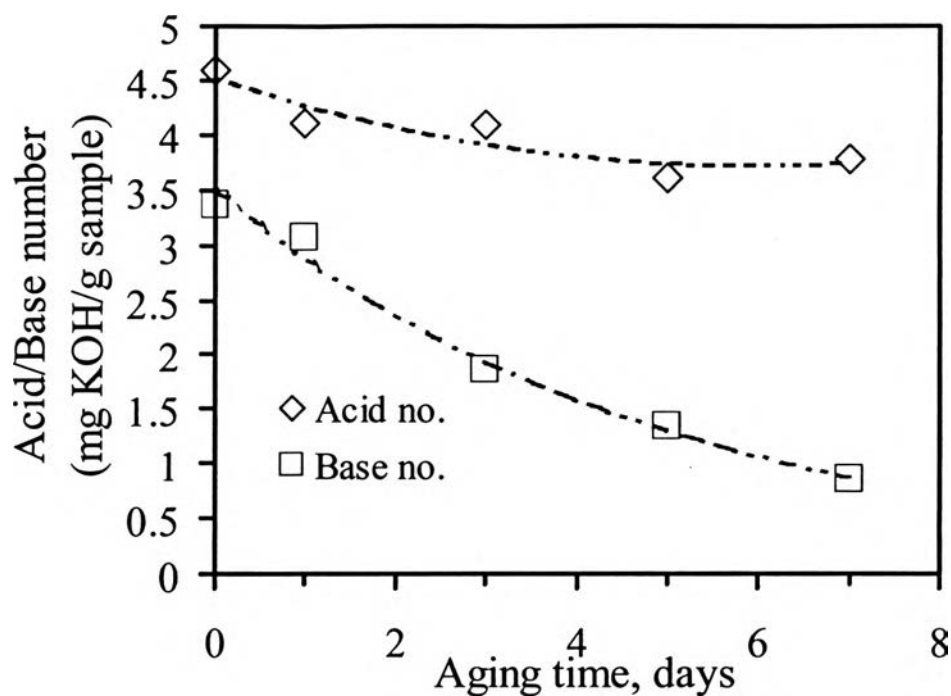


Figure 4.13 Relationship between acid/base number of asphaltene at constant aging temperature of 120 °C under nitrogen environment

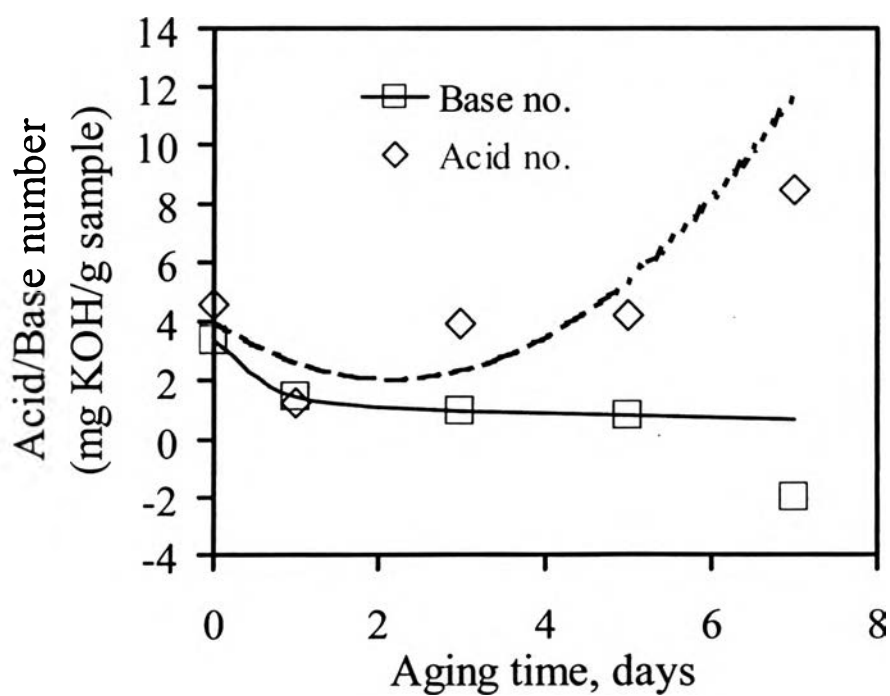


Figure 4.14 Relationship between acid/base number of asphaltene at constant aging temperature of 120 °C in air

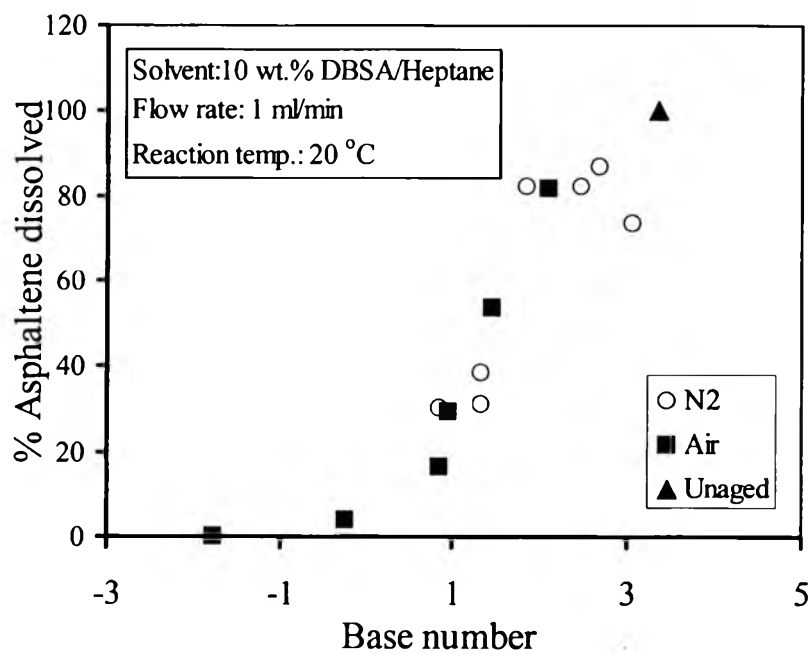


Figure 4.15 Relationship between the percentage of asphaltene dissolved and base number under different aging conditions

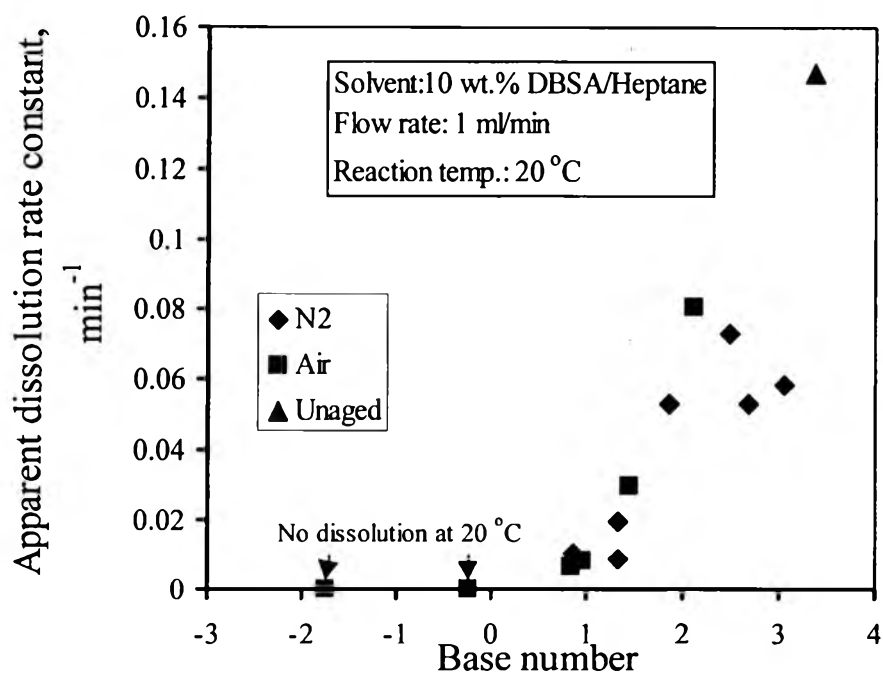


Figure 4.16 Relationship between apparent rate constant and base number under different aging conditions

As shown in Figure 4.17, there is no overall correlation between the percentage of asphaltene dissolved and its acid number. However, there are two possible correlations for two different aging media of nitrogen and air. The percentage of asphaltene dissolved increased with increasing its acid number for asphaltene aged under nitrogen contrary to one aged in air, which the percentage of asphaltene dissolved decreased when its acid number increased. Figure 4.18 shows the similar trend of the correlation between the apparent dissolution rate constant and the acid number of asphaltene aged under two different media. However, further study should be carried out to verify the relationship between the acid number and the dissolution of asphaltene.

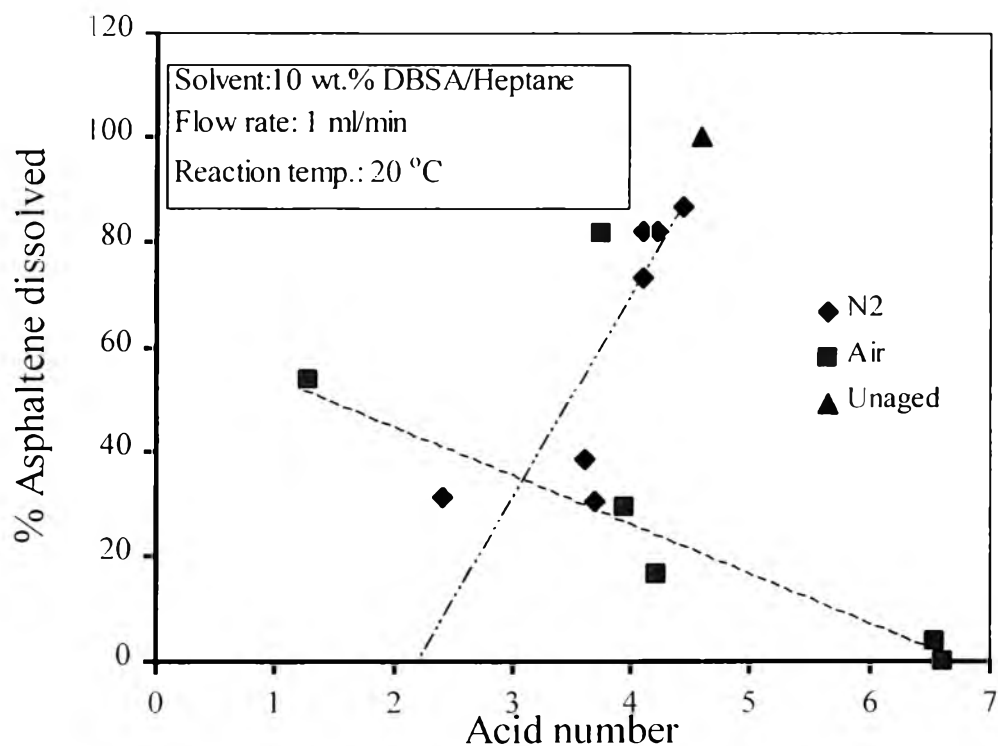


Figure 4.17 Relationship between the percentage of asphaltene dissolved and acid number

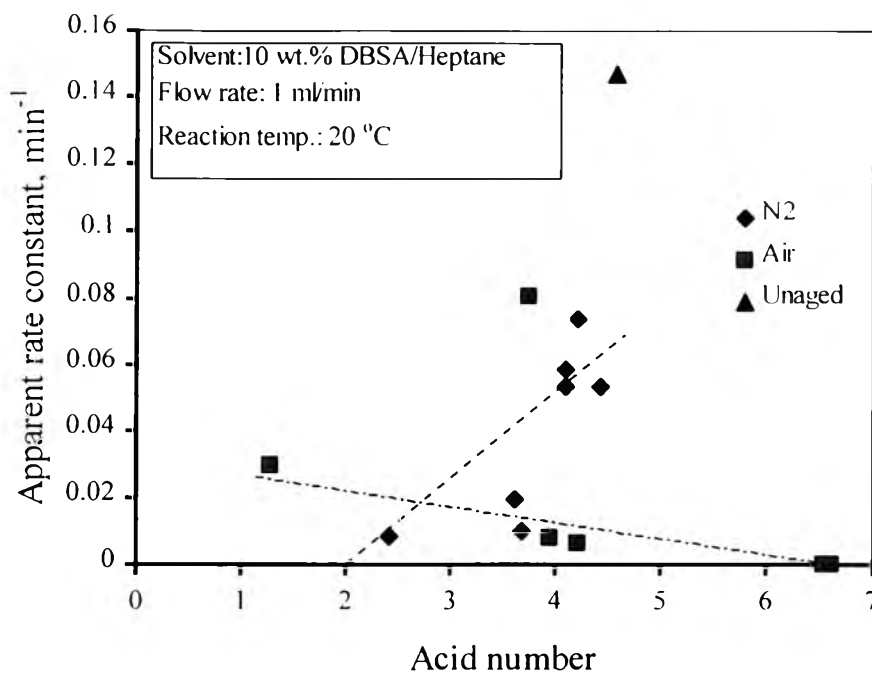


Figure 4.18 Relationship between apparent rate constant and acid number

4.4 Determination of Asphaltene Structure

4.4.1 Elemental Composition Analysis

Elemental analysis of five asphaltene samples aged at different conditions was performed in order to investigate the change of the asphaltene composition. The five samples of asphaltenes, unaged, 120°C with 7 days under N₂, 150 °C with 3 days under N₂, 120°C with 5 days in air and 150 °C with 3 days in air, have different compositions as shown in Table 4.1. Since other compositions could not be determined by this equipment, oxygen content was roughly estimated by subtracting with weight % of these three fractions. Table 4.1 shows the ratios of H, N and O to carbon and the percent change from that of unaged sample. From the results, it confirms that under nitrogen environment, the condensation reaction occurs affecting the reduction in the H:C ratio. In contrast, the ratio of O/C of asphaltene samples aged in air

Table 4.1 Ratios of hydrogen, nitrogen and oxygen to carbon of five asphaltene samples aged at different conditions

Asphaltene	H/C	% change	N/C	% change	O/C	% change
Unaged	0.0972	-	0.0224	-	0.0925	-
120 °C 7 days N ₂	0.0965	-0.727	0.0229	2.221	0.1064	14.999
150 °C 3 days N ₂	0.0972	-0.007	0.0229	1.904	0.0935	1.088
120 °C 5 days Air	0.0961	-1.073	0.0232	3.408	0.1095	18.381
150 °C 3 days Air	0.0919	-5.436	0.0238	5.972	0.1240	33.982

increased significantly. The results firmly indicate that the oxidation reaction occurs during aging process in air.

4.4.2 Functional Group Analysis

FT-IR spectra of asphaltenes aged under different conditions are shown in Figures 4.19-4.21. The spectra indicate significant increases in all functional groups of aged asphaltenes. An increase in intensity of a wide band around 3300 cm^{-1} , which represents either acidic or phenolic compounds particularly in the asphaltene aged in air, is consistent with the results from acid-base titration and elemental analysis. It confirms the occurrence of the oxidation reaction during aging in air.

Other important ranges are the absorption at $3,040\text{ cm}^{-1}$ and at $1,452, 1,495, \text{ and } 1,607\text{ cm}^{-1}$ indicating the aromatic C-H stretch and aromatic C=C stretch, respectively. From Figure 4.21, all functional groups of asphaltenes aged in air are larger than those of asphaltenes aged under nitrogen.

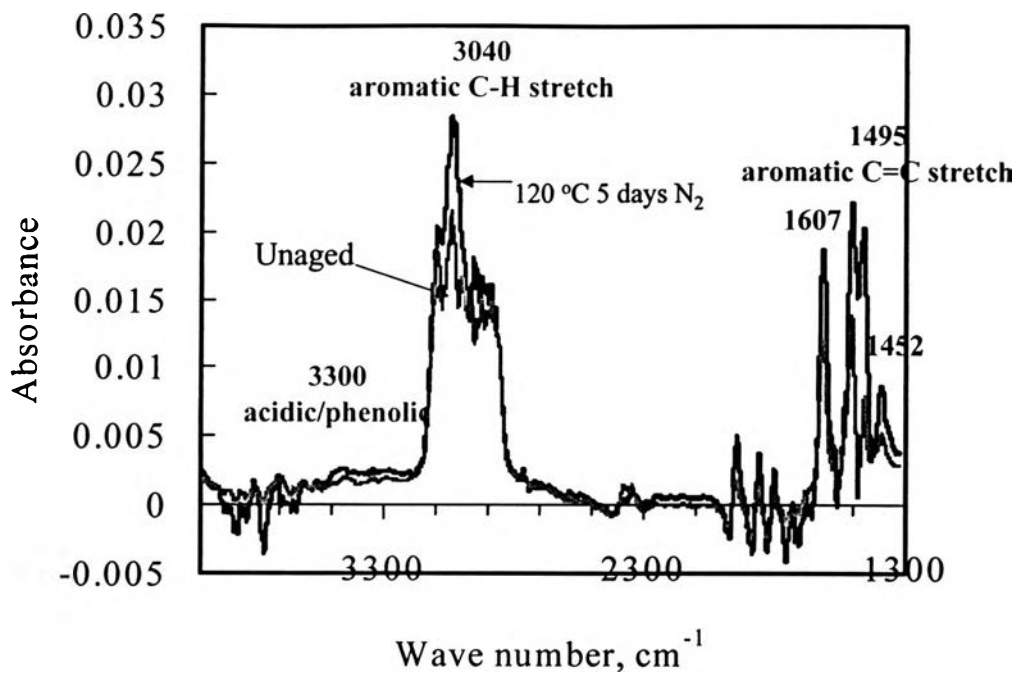


Figure 4.19 The FT-IR spectra when aged under nitrogen environment in comparison with unaged asphaltene

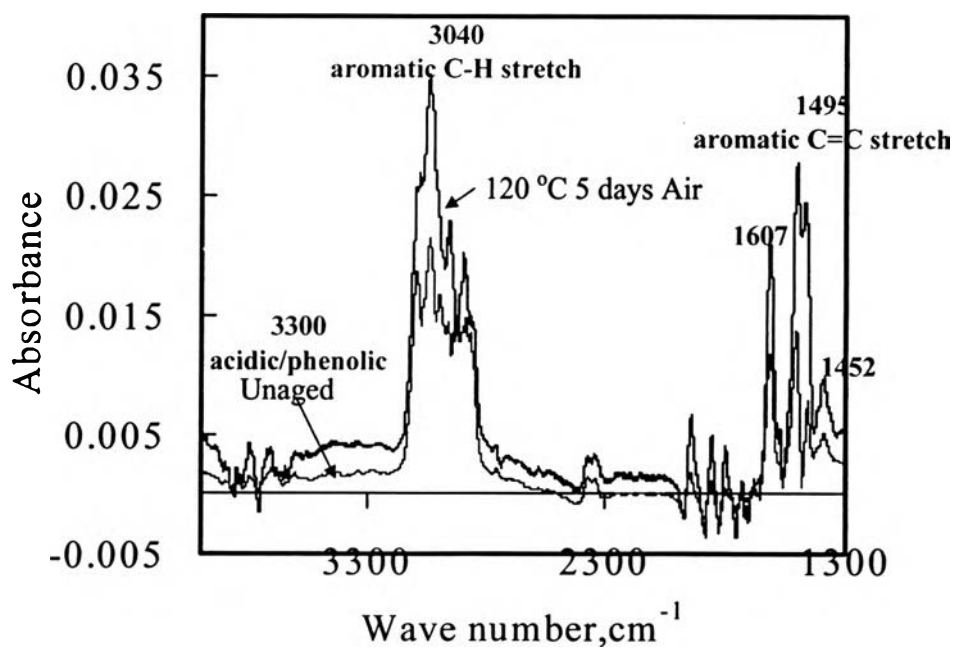


Figure 4.20 The FT-IR spectra when aged in air in comparison with unaged asphaltene

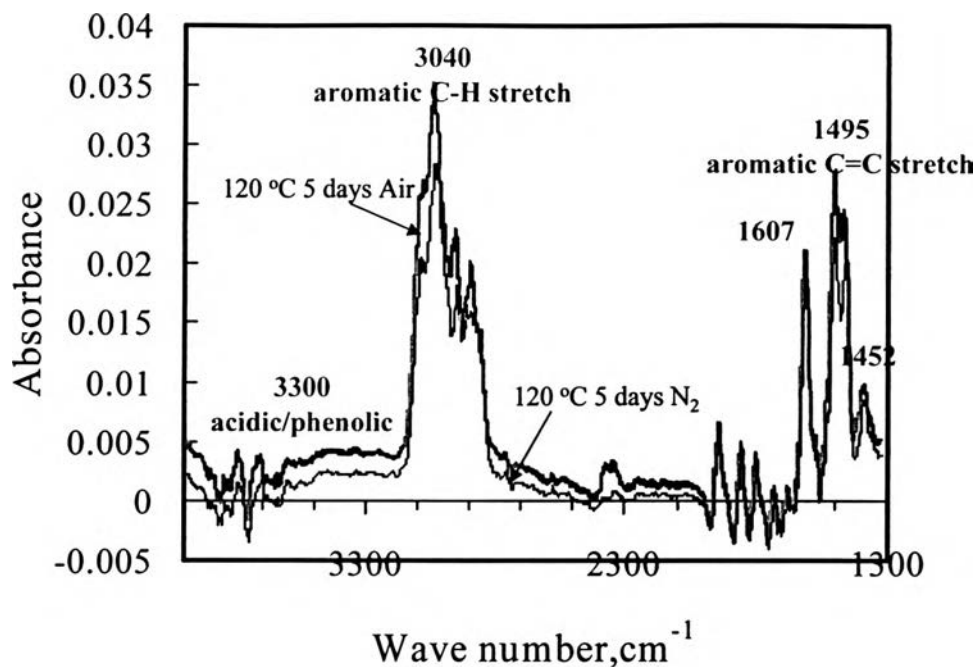


Figure 4.21 The FT-IR spectra comparing between asphaltene aged under nitrogen and asphaltene aged in air

4.4.3 Molecular Weight Analysis

Molecular weights of selected aged and unaged asphaltenes were determined by Gel Permeation Chromatography using pyridine as a solvent at 80° C. Table 4.2 shows that the molecular weight of asphaltene increases significantly after aging. The molecular weight distributions of four asphaltene samples are shown in Figure 4.22. The average molecular weights of aged asphaltene are much higher than that of unaged asphaltene. These results confirm the hypothesis about the occurring of the condensation polymerization reaction.

Table 4.2 Molecular weights of asphaltene samples under different aging conditions

Aging conditions	Molecular weights of asphaltene samples		
	Mn ¹	Mw ²	Mz ³
Unaged	1310	22100	177400
3-days at 150 °C under N ₂	1040	49500	479600
7-days at 120 °C under N ₂	1360	79600	891000
5-day at 120 °C in Air	1840	68100	883200

¹ The number average molecular weight

² The weight average molecular weight

³ The z average molecular weight

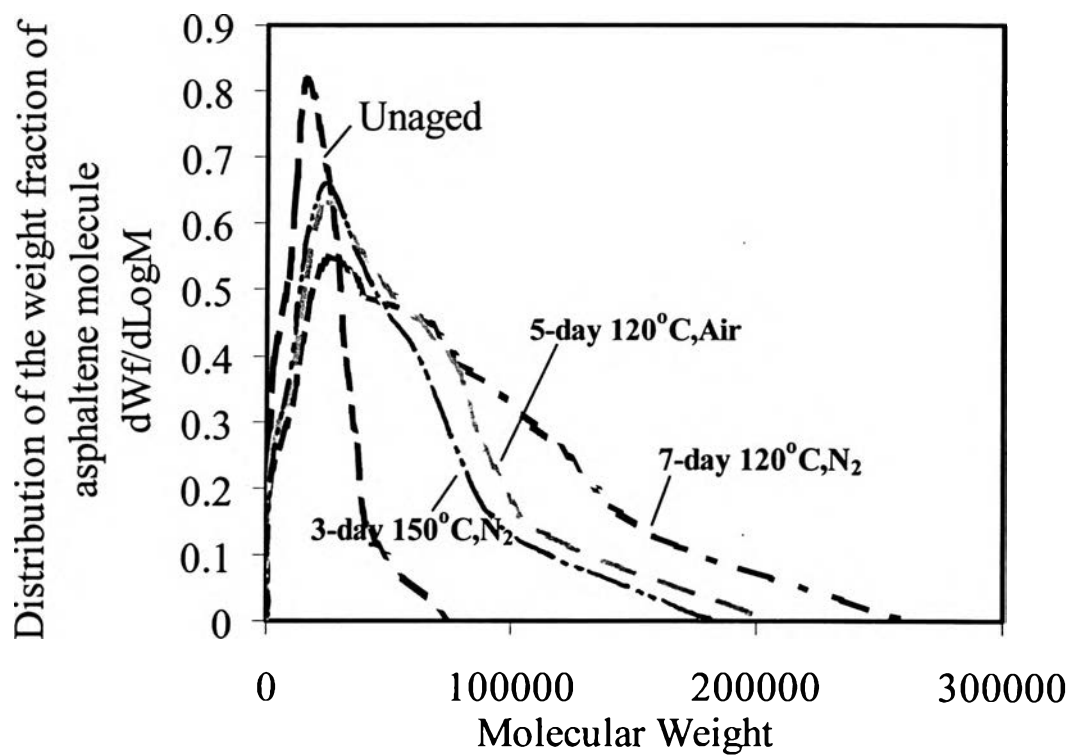
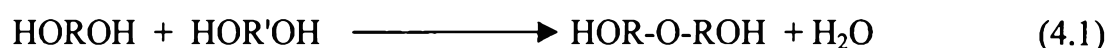


Figure 4.22 Molecular weight distribution of Zuata asphaltene at different degree of aging

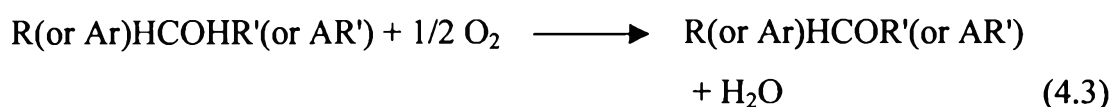
4.4.4 Proposed Chemical Transformation During Thermal Aging Process

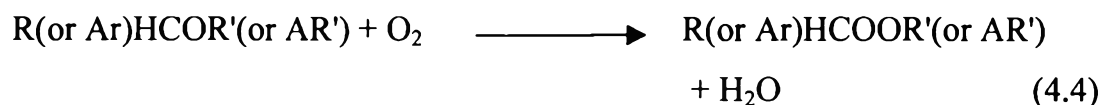
The results from the dissolution study, acid/base titration and the asphaltene structure analysis are consistent with the work studied by Soontravanich (1999) that the carbonyl group occurred during aging process in air. It can be explained by two simultaneous reaction of condensation and oxidation.

Condensation polymerization can occur by two asphaltene molecules react with each other through the O-O bond to produce one molecule of acid anhydride and water resulting in the reduction of acid sites. The other reaction amine group of one asphaltene molecule reacts with the carbonyl group of another molecule to produce higher molecular weight asphaltene molecule and a molecule of water resulting in the reduction of acid and base sites. These two condensation reactions are described below.



Oxidation reaction appears in conjunction with condensation polymerization when asphaltene was aged in air. Based on the FTIR results and the elemental analysis results, the hydroxyl group in asphaltene molecules reacts with oxygen to form ketone or aldehyde by releasing a water molecule. The product can be further oxidized to form ester or carboxylic acid. Consequently, it results in increasing acid sites. These two steps of oxidation reaction are.





Based on the results from the acid/base titration described before, for asphaltene aged in air and at low temperature (20°C - 90°C), the condensation reactions had dominated the whole system. When aging temperature exceeded 120 °C, the oxidation reaction became predominant resulting in increasing the acid number but decreasing the base number.

For the case of asphaltene aged in air, it was quite clear that the oxidation reaction became predominant. This conclusion was clearly supported by the results of both the elemental analysis and the FTIR spectra.