CHAPTER IV
RESULTS AND DISCUSSION

4.1 Composition and Fractionation of Original Asphaltenes

The original asphaltenes were obtained from COL-2 crude oil, Venezuela by diluting the crude with heptane as mentioned in Chapter III. The average yield of asphaltenes was approximately 7.24 mg/ml of crude oil. The appearance of this precipitate was dark brown.

The asphaltenes obtained from precipitation were then fractionated into subfractions having different polarities. The first fraction, F60/40, which came out by adding pentane (60% by volume) to a solution of asphaltene and methylenechloride is the most polar fraction. Then the volume ratio of pentane to dichloromethane was subsequently increased to 70:30, 80:20, and 90:10 and the precipitates collected in each step were named F70/30, F80/20, and F90/10, respectively. Figure 4.1 shows the yield of various fractions obtained from Col-2 asphaltenes. One can see from Figure 4.1 that the F70/30 has the highest fraction yield, which indicates that Col-2 crude oil possesses relatively high polar fraction of asphaltenes.

4.2 Morphology of Different Fractions of Original Asphaltenes

The morphology of original asphaltenes obtained from Col-2 crude oil was observed using Scanning Electron Microscope, SEM. As can be seen from Figure 4.2, the SEM images reveal the amorphous structure of original asphaltenes.

As can be seen in Figure 4.3, fraction 1 (F60/40), the most polar one, has smooth surface which indicates its ordered structure. In contrast, Fraction

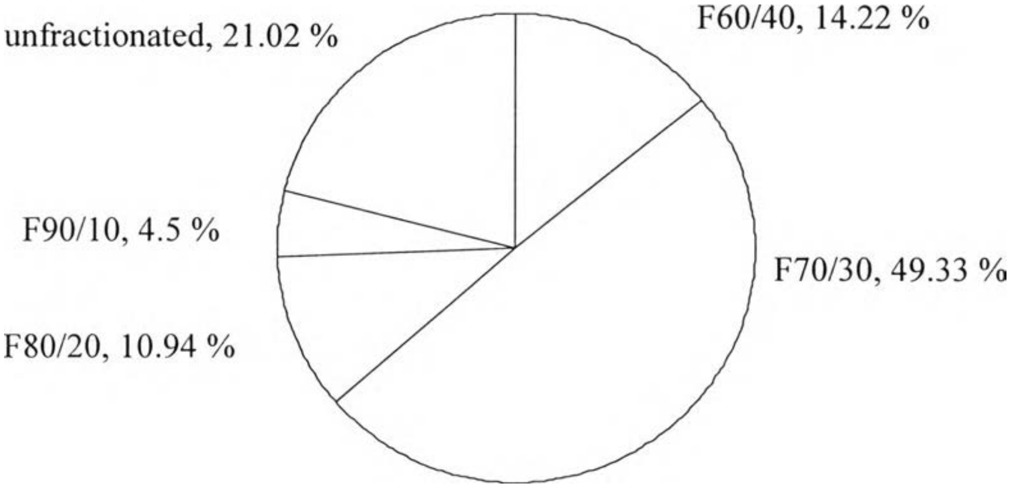


Figure 4.1 The fractionation yield of COL-2 asphaltenes

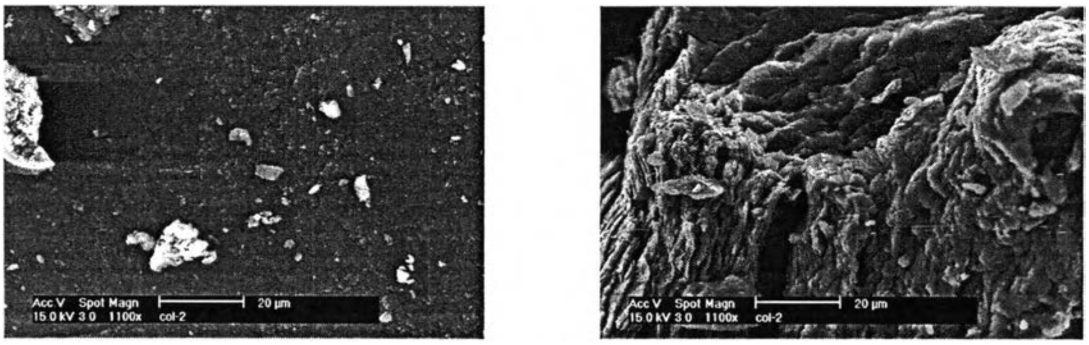
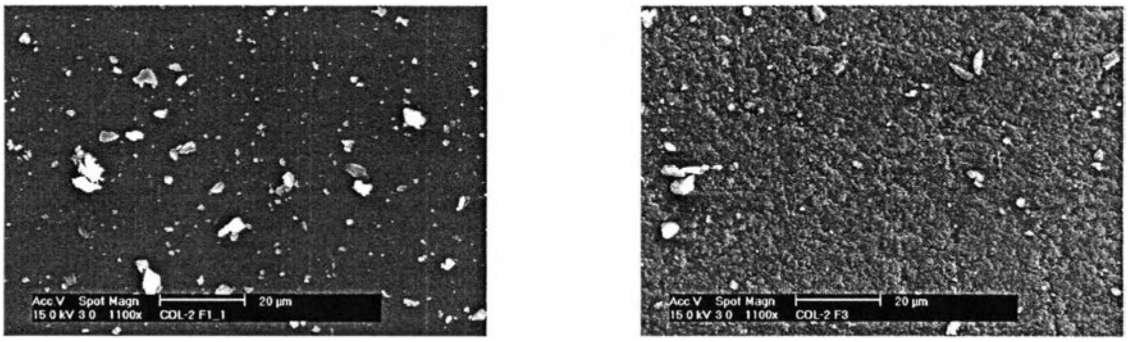


Figure 4.2 SEM images of asphaltenes in different view (1100X)

3 (F80/20), less polar one, shows relatively rough surface compared to fraction 1. Asphaltene subfractions can be simply distinguished from their surface



(a) Fraction 1 (F60/40)

(b) Fraction 3 (F80/20)

Figure 4.3 SEM images of asphaltene subfractions (1100X)

structure. The less polar asphaltenes seem to have more amorphous structure as comparEd to the more polar ones.

4.3 Thermal Aged Asphaltenes

Asphaltenes were conditioned at 22, 80, 120, and 150 °C in a vacuum oven which was maintained at a vacuum pressure of 15 in Hg for different aging times ranging from 1 to 5 days. The samples of the original asphaltenes were aged at different temperatures and times in order to determine the effects on asphaltenes dissolution kinetics as well as morphology.

4.3.1 Effects of Aging Time on Asphaltene Dissolution

The samples of the original asphaltenes under the thermal aging treatment at 120 °C with different aging times were taken for the dissolution kinetics study. Two dissolution solvents of toluene and the micellar fluid containing 10 wt. % DBSA in heptane were used for the dissolution kinetics study. Figures 4.4 and 4.5 show the evolution of dissolved asphaltenes as a function of time at room temperature of 22 °C for both two dissolving fluids. The results showed that the rate of asphaltenes dissolution decreased with increasing the aging time. For the unaged asphaltenes, both solvents of DBSA containing heptane and toluene were effective in dissolving asphaltenes. After the thermal aging treatment, heptane containing 10 wt. % DBSA was better than toluene in dissolving the aged asphaltenes. The data obtained from Figures 4.4 and 4.5 were then replotted in terms of logarithm of undissolved asphaltenes mass fraction ($\ln M/M_0$) versus time as shown in Figures 4.6 and 4.7 respectively. The apparent dissolution rate constant, k, was simply calculated from the slope of linear fitting between $\ln (M/M_0)$ versus time. As can be seen from both Figures 4.6 and 4.7, the value of the apparent dissolution rate constant decreased with increasing the aging time for both dissolving fluids. The apparent dissolution rate constant of unaged and 5-day aged asphaltenes using DBSA/heptane solvent were found to be 0.3414 and 0.0408 min^{-1}, respectively while the values with toluene were 0.3857 and 0.0093 min^{-1}, respectively. From the values of the apparent dissolution rate constant at a given aging time, aging time affected significantly the dissolution property of asphaltenes and heptane containing 10 % DBSA was a better solvent than toluene.

Figure 4.8 compares the values of the dissolution rate constants at different aging times for both dissolving fluids of toluene and DBSA/heptane. A significant decrease of the dissolution rate constant appeared at the first day of aging and after the first day the value of the dissolution rate constant decreased slightly as an increase in the aging time.

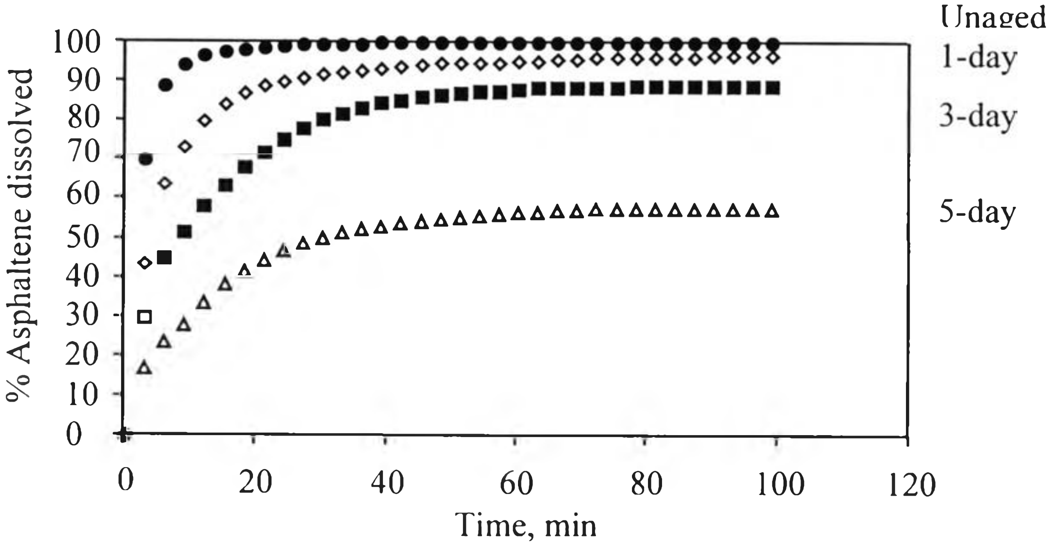


Figure 4.4 Evolution of asphaltene dissolved in 10 wt. % DBSA/heptane as a function of different aging times at aging temperature of 120 °C

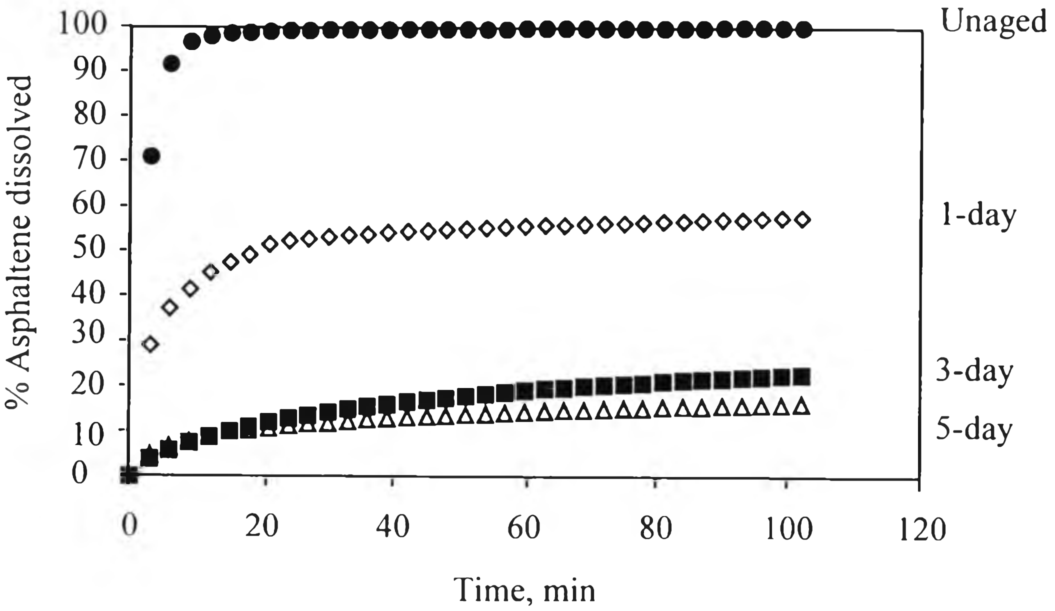


Figure 4.5 Evolution of asphaltene dissolved in toluene as a function of different aging times at aging temperature of 120 °C

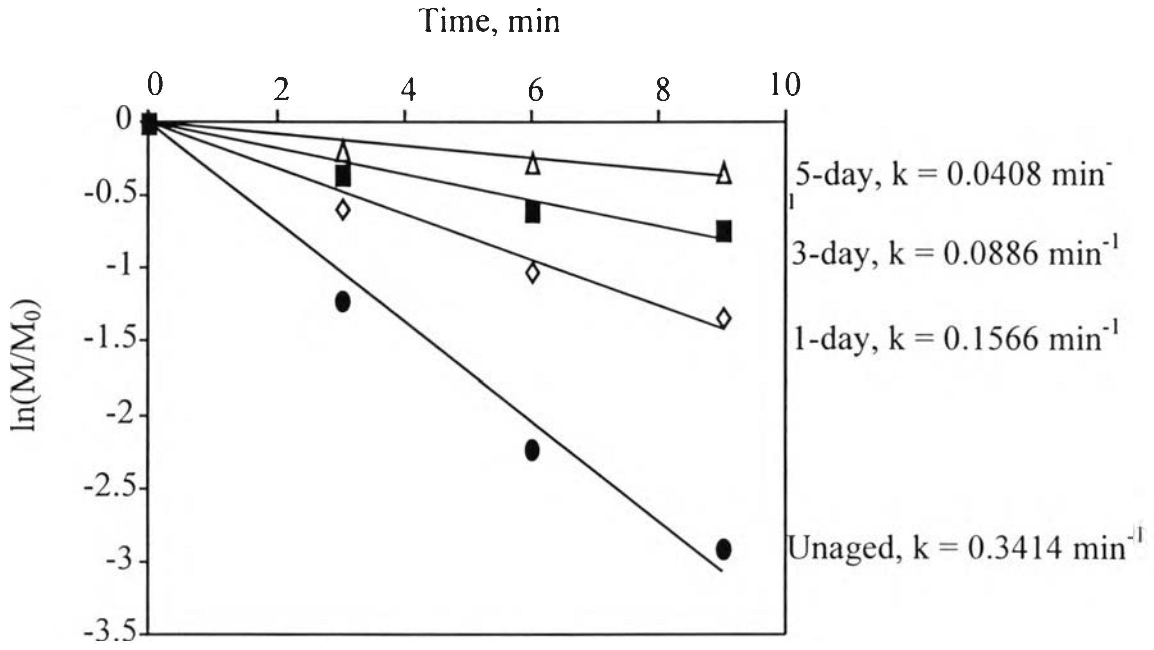


Figure 4.6 Plot of ln(M/M_0) versus time of aged asphaltenes at 120 °C and different aging times with 10 wt. % DBSA/heptane as dissolving fluid at 22 °C

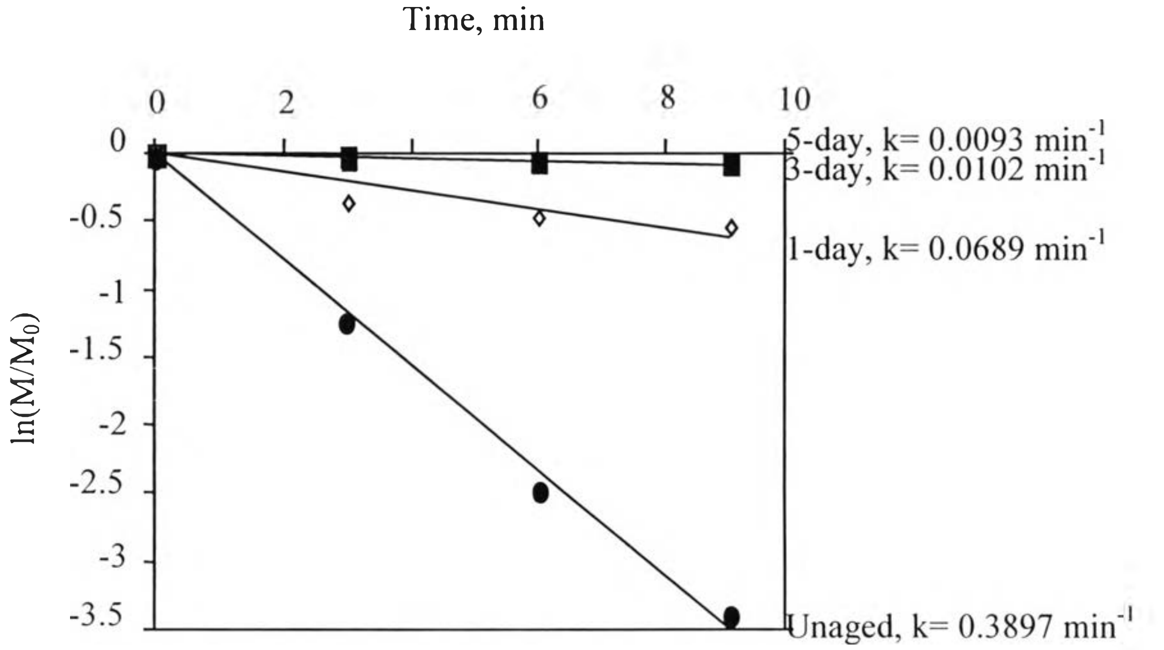


Figure 4.7 Plot of ln(M/M_0) versus time of asphaltenes aged at 120 °C and different aging times with toluene as dissolving fluid at 22 °C

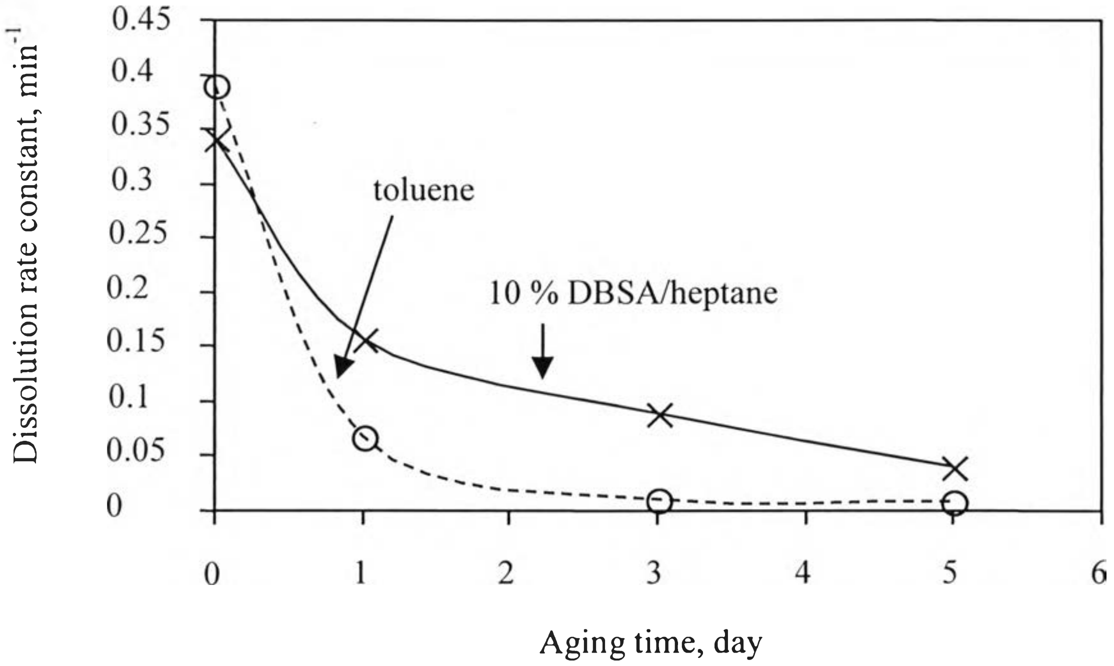


Figure 4.8 Dissolution rate constant as a function of aging time for asphaltene aged at 120 °C using toluene and DBSA/heptane as dissolving fluids

4.3.2 Effects of Aging Temperature on Asphaltene Dissolution

Aging temperature is another important parameter which affects the aging process. In this study, reservoir temperatures were varied from 22 to 150°C. The asphaltenes aged at a higher temperature are dissolved slower both in DBSA/heptane system and in toluene as shown in Figures 4.9 and 4.10. These results indicate that asphaltenes which are aged at a high temperature for a long time, create severe problems in asphaltene remediation.

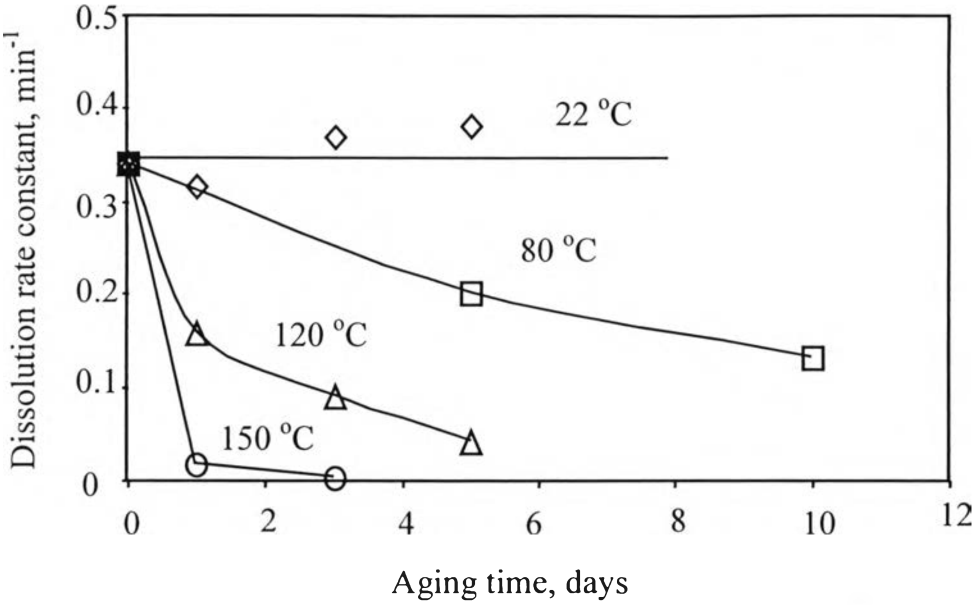


Figure 4.9 Comparison of dissolution rate constants as a function of aging time of asphaltene aged at different temperatures (Solvent : 10 wt. % DBSA/heptane)

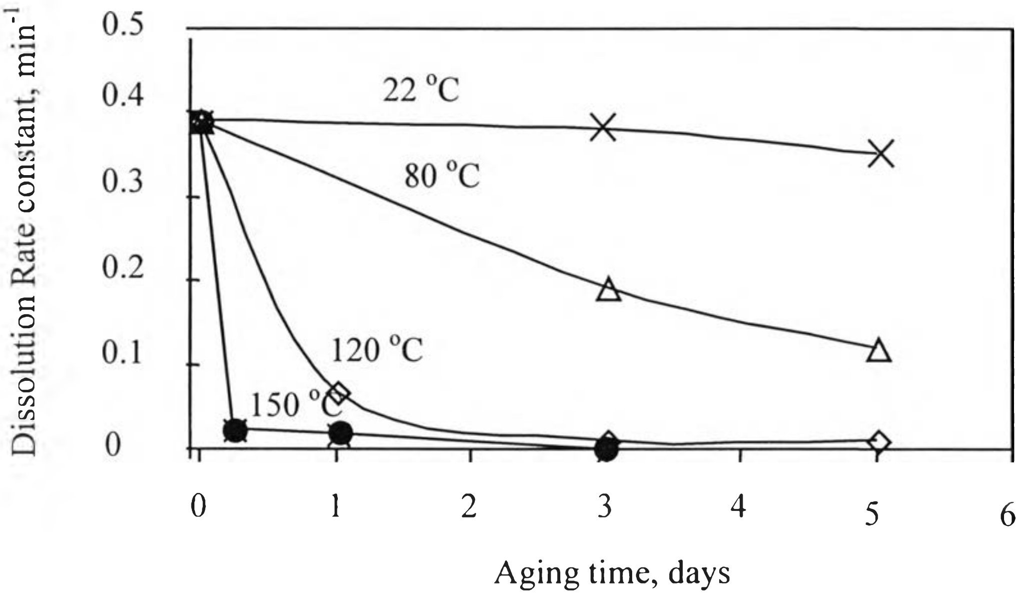


Figure 4.10 Comparison of dissolution rate constants as a function of aging time of asphaltene aged at different temperatures (Solvent : toluene)

4.4 Fractionation Study of Aged Asphaltenes

Aged asphaltenes were fractionated into three subfractions by following the same procedure described in Chapter III. The ratios of pentane to methylenechloride were changed to 60/40, 80/20, and 90/10 instead of 60/40, 70/30, 80/20 and 90/10. The initial ratio of asphaltene to methylenechloride was also changed to 1:50 (by wt.) in order to ensure that all of the asphaltenes were totally dissolved in the solvent. Figure 4.11 shows the yields of various subfractions of unaged and aged asphaltenes. It was found that high polar subfractions increased in amount when aging. This indicates that some changes in the chemical structure of asphaltenes takes place during aging and some chemical reactions also take place which alter the polarity of the asphaltenes molecules during aging.

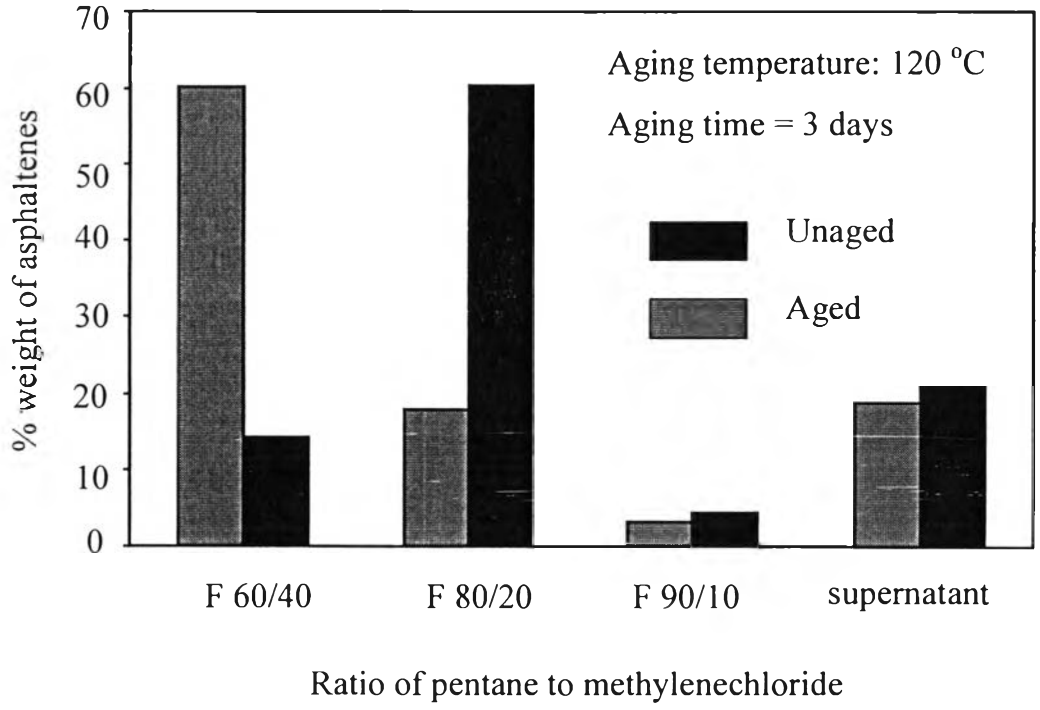
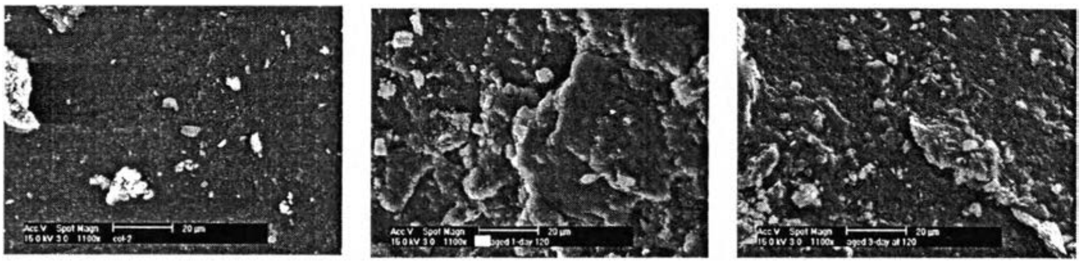


Figure 4.11 Effect of aging on asphaltene subfractions

4.5 Morphology of Aged Asphaltenes

The aged asphaltenes have less ordered structure than unaged ones as shown in Figure 4.12. Amorphous-like structure that was shown in the aged asphaltene is due to the loss of small molecules during aging process. It was also observed that the morphology of asphaltenes had been changed during thermal aging process. The results indicate that the chemical structure of asphaltenes have been changed during thermal aging process.



(a) Unaged (b) 1-day at 120 °C (c) 3-day at 120 °C

Figure 4.12 Comparison of surface structures between unaged and aged asphaltenes (1100X)

4.6 Chemical Structure of Aged Asphaltenes

4.6.1 Analysis Results of Functional Groups

Fourier transform spectroscopy was performed to identify the functional groups of asphaltenes. A Mattson Instruments Galaxy Series 7020-A FTIR spectrophotometer was operated at a setting of 100 scans at 2 cm^{-1} by using diffuse reflectance infrared Fourier transform (DRIFT). The samples were prepared by mixing asphaltene with KBr (IR grade) in a ratio of 1 to 100 by wt.

FTIR spectra for unaged and aged asphaltenes are shown in Figures 4.13 and 4.14. Table 4.1 shows absorption peaks of some functional groups which are used as reference. The spectra indicate that there is an emergence of absorbance peak at 1680 cm^{-1} in aged asphaltenes especially with the samples that were aged at higher temperature. This peak indicates the presence of carbonyl group (Ege, 1989). The absorption at this peak can indicate both ketone and ester groups which may be conjugated with double bond or aromatic ring. The strong and sharp absorption between 1600 and 1450 cm^{-1} and between 850 and 700 cm^{-1} indicates the presence of aromatic rings (Ege, 1989). There was also a slight increase in the amount of aromatic ring indicated at 1600 and 1450 cm^{-1}. It can also be seen clearly that the aliphatic CH_2 and CH_3 groups at 2850 and 2920 cm^{-1} decreased with aging temperature and aging time.

The possible reactions during aging are the oxidation of hydroxyl group (-OH) to carbonyl functional group and that of carbonyl group to ester.

$$\text{R(or Ar)HCOHR'(or Ar')} + 1/2O_2 \longrightarrow \text{R(or Ar)COR'(or Ar')} + H_2O \qquad (4.1)$$

$$\text{R(or Ar)COR'(or Ar')} + O_2 \longrightarrow \text{R(or Ar)COOR'(or Ar')} + H_2O \qquad (4.2)$$

These oxygen-containing functional groups are responsible for higher polarity of asphaltene molecules.

Table 4.1 IR absorption peak of asphaltenes (Ege, 1989)

Wavenumber (cm^{-1})	Type of functional group
3500-3300	NH, OH stretching, and H-bonding
3050-3000	Aromatic stretching (C-H)
2950	CH_3-stretching
2920, 2850	Aliphatic CH_2-stretching
1720-1690	Aldehyde, ketone and acid
1650-1630	C=O highly conjugated
1600	Aromatic or C=C stretching
1450	CH_2 and CH_3 bending
1375	Systemetric C-CH_3 bending
1300-1100	C-O stretching and O-H bending in Phenoxy structures, ethers
860	Isolated aromatic H
833	1, 4 substituted aromatic groups

4.6.2 Molecular Weight of Aged Asphaltenes

Molecular weight of aged and unaged asphaltenes were measured by Gel Permeation Chromatography using Pyridine as a solvent at 80 °C. Figure 4.15 shows a significant change in the molecular weight distribution of unaged and aged asphaltenes which were aged at 120 °C for 1 to 5 days. The averaged molecular weights of the aged asphaltenes are higher than that of unaged ones as shown in Table 4.2. For aged asphaltenes, the number fraction of molecules which has molecular weight ranging between 8,000 and 30,000 is less than that of the unaged one, but there is an increase in the fraction which has higher

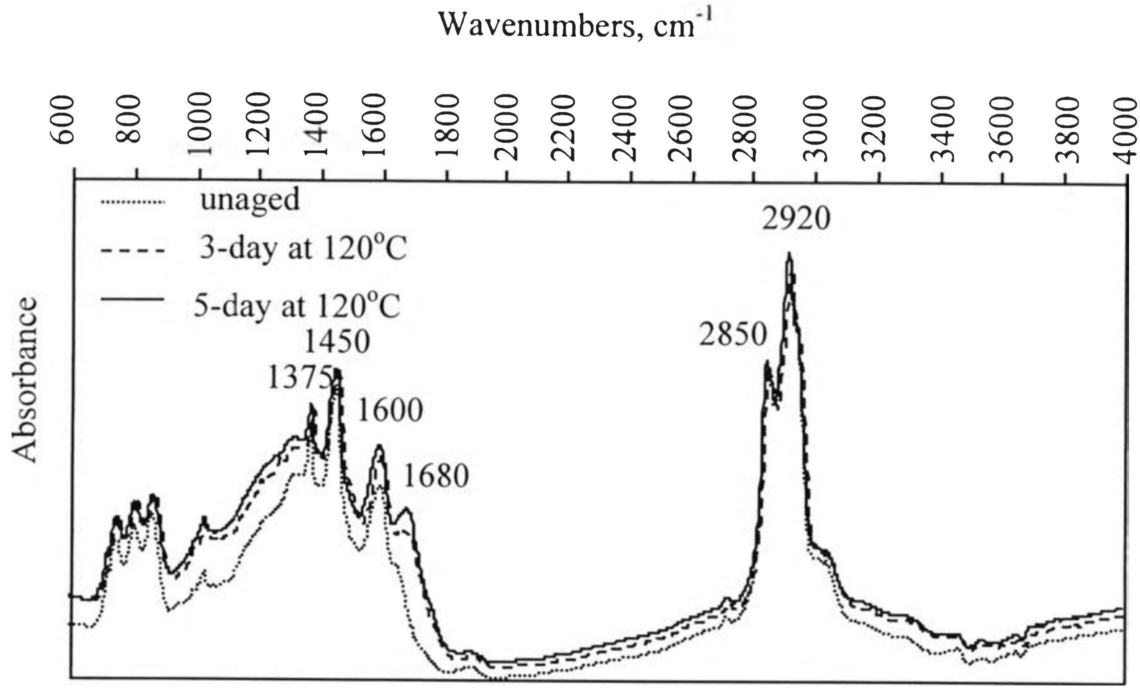


Figure 4.13 FTIR spectra of unaged and aged asphaltenes (with different aging times)

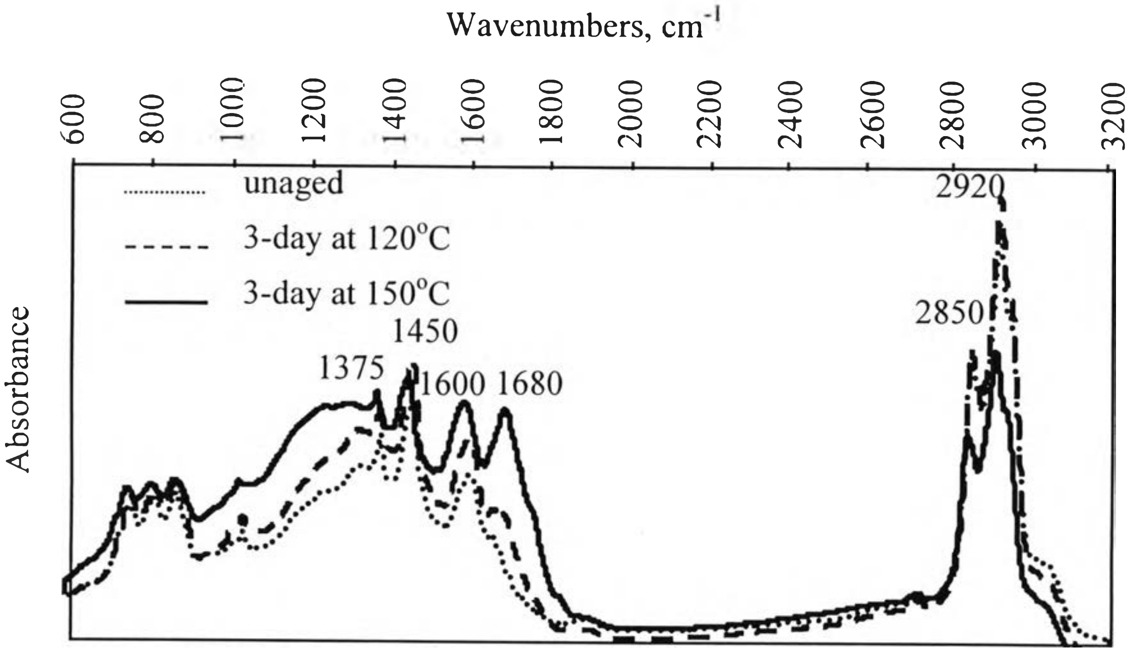


Figure 4.14 FTIR spectra of unaged and aged asphaltenes (with different aging temperatures)

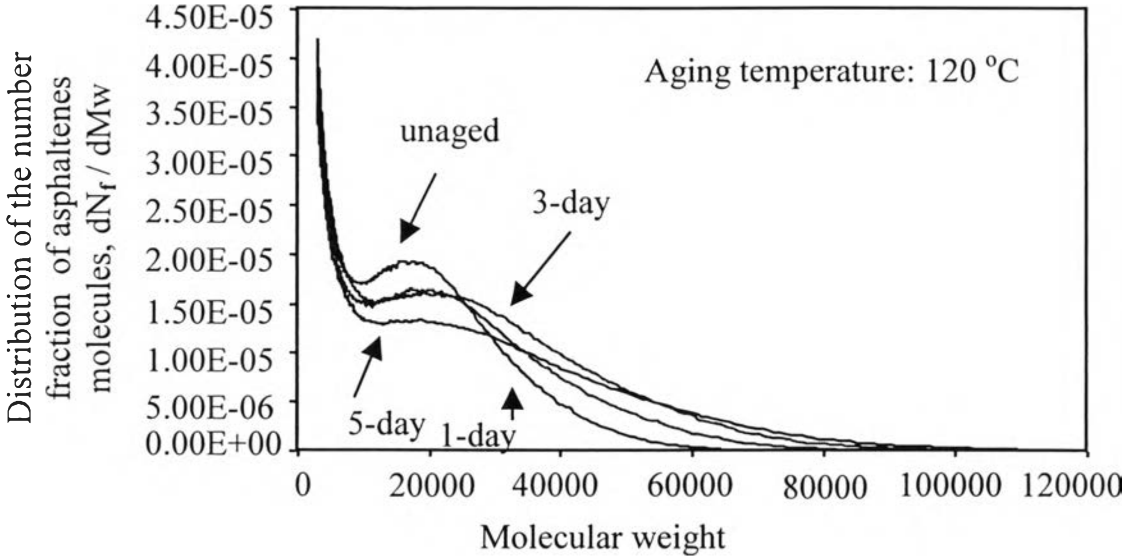


Figure 4.15 Molecular weight distribution of unaged and aged asphaltenes at different aging time

Table 4.2 Comparative molecular weight between unaged and aged asphaltenes

Asphaltene	Mn[1]	Mw[2]	Mz[3]
Unaged	350	15500	59400
3-day at 22 °C	1090	17000	60500
1-day at 120 °C	460	20400	78900
3-day at 120 °C	770	24600	102900
5-day at 120 °C	500	26900	116300

[1] Mn = a number average molecular weight

[2] Mw = a weight average molecular weight

[3] Mw = an average molecular weight

molecular weight ranging from 30,000 to 100,000 in the aged asphaltenes. It is noticed that there is no significant difference of the fraction of molecule in the low range molecular weight (below 500). It can be inferred that asphaltene molecules polymerize into larger molecules during aging process yielding an increase in molecular weight. The degree of polymerization was higher for the samples aged for a longer aging time and at a higher aging temperature.

4.6.3 Results of Elemental Analysis of Aged Asphaltenes

Unaged and aged asphaltenes were analyzed for determining carbon, hydrogen, sulfur, and nitrogen contents using an elemental analyzer. The element contents (wt. %) and their mole ratio are presented in Table 4.3. The analysis results showed that C/H ratio of asphaltenes increased significantly during aging process. One of the possible reasons for increasing in C/H ratio would be the loss of hydrogen during polymerization and oxidation reaction. It is very interesting to point out that oxygen content and the O/C ratio increased significantly during aging process. The results simply imply that oxidation reaction is responsible for increasing oxygen content.

Table 4.3 Percent element and mole ratio for unaged and aged asphaltenes

Asphaltene	Element Percent					Mole Ratio	
	C	H	O	N	S	C/H	O/C
Unaged	86.43	7.33	1.17	1.66	3.13	0.98	0.01
3-day at 120 °C	85.33	6.93	2.13	1.85	3.10	1.03	0.02
1-day at 150 °C	84.37	6.66	3.16	1.78	3.10	1.06	0.03
3-day at 150 °C	81.79	6.12	5.87	1.75	3.03	1.11	0.05

4.7 Possible Reactions during Thermal Aging Process

4.7.1 Oxidation

Even though the aging process was conducted under vacuum pressure, the FT-IR spectra showed that there was an increase in carbonyl functional group taking oxygen during aging process. The percentage of oxygen obtained from elemental analysis also confirmed that there is an increase in the amount of oxygen during aging. The oxidation of asphaltene may follow as,

$$\text{R(or Ar)HCOHR'(or Ar')} + 1/2O_2 \longrightarrow \text{R(or Ar)COR'(or Ar')} + H_2O \qquad (4.3)$$

Hydroxyl group in asphaltene molecules reacts with oxygen to form ketone by releasing a water molecule. The product of this reaction can be further oxidized to form ester.

$$\text{R(or Ar)COR'(or Ar')} + O_2 \longrightarrow \text{R(or Ar)COOR'(or Ar')} + H_2O \qquad (4.4)$$

The oxidation reaction may be responsible for uptaking oxygen molecule to the asphaltene molecule which corresponds to the result from elemental analyzer which shows an increase in the amount of oxygen as the asphaltenes is aging.

The carbonyl group is more polar than hydroxyl group by nature. Increases in both carbonyl and ester in asphaltenes contribute to the higher polarity of asphaltenes.

The solubility parameter (Altgelt and Boduszynski, 1994), introduced by Hildebrand and Scott, is the square root of the energy of vaporization, ΔE_V, over the molar volume, V_M.

$$\delta = \left(\frac{\Delta E_v}{V_M} \right)^{1/2} \tag{4.5}$$

$$\Delta E_V = \Delta E_D + \Delta E_P + \Delta E_H \tag{4.6}$$

The energy of vaporization, ΔE_V, is the sum of three factors which are hydrogen bonding, ΔE_H, permanent-dipole-permanent-dipole interactions, ΔE_P, and nonpolar London dispersion forces, ΔE_D.

So the solubility decreases with an increase in

a) Polarity
b) Dipole interactions due to aromatic rings and heteroatoms
c) Molecular size

In this case, the asphaltene solubility decreased because of its higher polarity due to the increase in the carbonyl group.

The oxidised asphaltene has less solubility both in toluene and DBSA/heptane system which means that the oxidized asphaltene creates severe problems during asphaltene remediation.

4.7.2 Polymerization

During aging process, the asphaltene deposits tend to polymerize and release light molecules (like water, ammonia, hydrogen sulfide, etc.). The evidence is shown in the change of molecular weight distribution.

It is strongly evident that condensation polymerization is a major reaction responsible for an increase in the molecular weight.

$$\text{ROH} + \text{R'(or Ar')OH} \xrightarrow{\Delta} \text{R-O-R'} + H_2O \tag{4.7}$$

$$\text{HOROH} + \text{OHR'OH} \xrightarrow{\Delta} \text{HOR-O-ROH} + H_2O \tag{4.8}$$

Higher molecular weight asphaltenes have less solubility which can be explained from solubility parameter as be supported from the results of the dissolution study.