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Effects of Temperature and Pressure on Asphaltene Particle Size Distributions in Crude Oils Diluted with *n*-Pentane

Bent B. Nielsen, William Y. Svrcek, and Anil K. Mehrotra*

Department of Chemical and Petroleum Engineering, The University of Calgary, Calgary, Alberta, Canada T2N 1N4

The effects of temperature (0–150 °C) and pressure (0–5.6 MPa) on the size distribution of asphaltene particles (or agglomerates), formed as a result of diluting the crude oils with *n*-pentane, were studied using a modified laser particle analyzer. Four crude oils, ranging from an asphaltic condensate to a heavy oil-sand bitumen, were tested in this investigation. The average size of asphaltene agglomerates ranged from 266 to 495 μm . The results suggest that the mean asphaltene particle size increases with pressure and decreases slightly with temperature; however, no trends were evident with the molar mass of crude oils. Although the particle size distributions in most cases were unimodal and described adequately by the log-normal distribution function, bimodal distributions were also identified in certain cases.

Introduction

Formation and deposition of asphaltene agglomerates is a major obstacle in the production of heavy oils and bitumens as well as during secondary and tertiary crude oil recovery operations. The formation of two phases in heavy oils, their incompatibility, and the size distribution of the precipitated asphaltene agglomerates are important interrelated phenomena which are not well understood at the present. Changes in temperature (Ali and Al-Ghanam, 1981), pressure (Burke et al., 1990; Park and Mansoori, 1988), composition (Nadirov et al., 1987; Katz and Beu, 1945), and electrical effects (Katz and Beu, 1945; Lichaa and Herrera, 1975) have been reported to cause asphaltene deposition in wells, pipelines, and production equipment. The presence of asphaltenes aggravates fouling of catalysts, coking, and promotion of emulsions during the processing of crude oils.

The purpose of this investigation was to examine the effects of temperature and pressure on the size of asphaltene particles or agglomerates that are formed when a crude oil is mixed with a paraffinic diluent. Four crude oils were tested with the average molar mass ranging from 114 kg/kmol for an asphaltic condensate to 522 kg/kmol for an oil-sand bitumen. The diluent used in all of the tests was 99.5% pure *n*-pentane, obtained from BDH.

The measurements were carried out at two pressures: 2.2 and 5.6 MPa. The effect of temperature at constant pressure was studied in 50 °C increments; from 0 to 150 °C using the two high-viscosity oils from Cold Lake and Lindberg (Alberta), while the two low-viscosity oils from Countess (Alberta) and the Border Gas Plant (British Columbia) were tested from 0 to 100 °C.

Nature of Asphaltenes and Their Agglomeration

Asphaltenes are a dark brown to black solid solubility class found in most crude oils. They are typically defined as being insoluble in either *n*-pentane or *n*-heptane but soluble in aromatic solvents (such as benzene and toluene), carbon disulfide, and chloroform (Lichaa and Herrera, 1975). Asphaltene residue may be precipitated from a crude oil by the addition of a nonpolar miscible solvent (for example, *n*-pentane or *n*-heptane). The chain length of the paraffin used determines the amount of residue

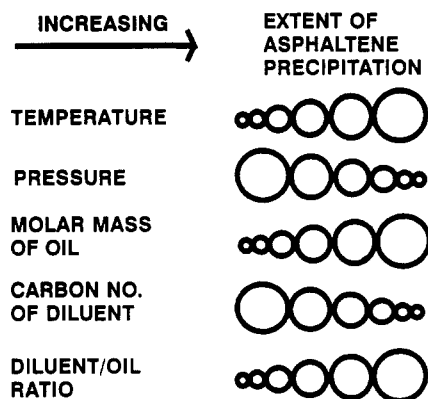


Figure 1. Qualitative relationship between the various parameters on the extent of asphaltene precipitation.

(Corbett and Petrossi, 1978; Mitchell and Speight, 1973), its degree of polarity (Speight, 1991), and the asphaltene particle size distribution (Ferworn, 1992). Typically, smaller molecules such as propane promote the deposition of more (but less polar) residue, while *n*-heptane causes precipitation of lesser amounts of a more polar residue. This trend is limited, as methane by itself will not cause deposition and molecules heavier than *n*-heptane do not appreciably promote a more polar or a decreased amount of residue (Mitchell and Speight, 1972).

The non-asphaltic fraction of a crude oil, often referred to as the maltenes, is comprised of oils, waxes, and resins. The difference in the amount of residuum obtained with propane and either *n*-pentane or *n*-heptane is referred to as the resins.

Crude oils consist of hydrocarbon components with a continuous distribution of molar mass (Champagne et al., 1985), including *in situ* gases and low molar mass hydrocarbons up to the highly polar, high molar mass asphaltene micelles. The solubility of heavier components in a crude oil is dependent on the relatively lighter components, whose solubility is in turn dependent on the still lighter components. This delicate balance suggests why asphaltenes are precipitated by disturbances to the solubility of the component species.

Changes in any of the several conditions can alter the thermodynamic stability of the crude oil. Figure 1 shows qualitatively the effects of varying the parameters on the extent of asphaltene precipitation. Increasing the temperature, the molar mass of the oil, or the diluent-to-oil

* Author to whom correspondence should be addressed.
E-mail: mehrotra@acs.ucalgary.ca.

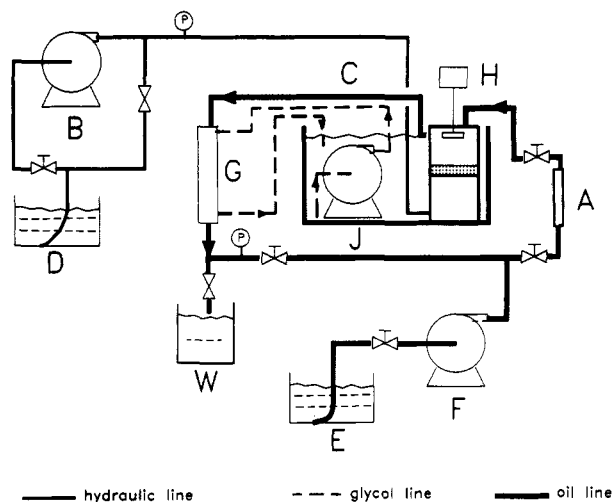


Figure 2. Schematic of high-pressure laser cell apparatus: A, bitumen reservoir; B, Gilson pump; C, glycol pump; D, hydraulic fluid reservoir; E, diluent reservoir; F, Jeffri pump; G, laser cell inside Brinkmann analyzer; H, pressure cell with stirrer; J, water bath; W, waste receptacle.

ratio results in larger amounts of asphaltene precipitate. Conversely, increasing the pressure or the number of carbon atoms in the diluent molecule results in a decreased extent of asphaltene precipitation. A brief discussion of the effects of some of the important variables on asphaltene precipitation is presented below.

Effect of Diluent Type and Ratio. The mean molar mass of the precipitated asphaltenes normally decreases when a shorter chain diluent is used (James and Mehrotra, 1988). This is because a lighter diluent precipitates more of the lower molar mass asphaltene fraction due to its lower solubility. An increase in the fraction of asphaltenes precipitated has been observed with increasing dilution ratio (Ali and Al-Ghannam, 1981; Burke et al., 1990; James and Mehrotra, 1988; Speight et al., 1984). The diluent-to-oil ratio also affects the asphaltene particle size distribution; Ferworn et al. (1993) and Funk (1979) found that asphaltene particle size increases with an increase in the dilution ratio at ambient pressure and temperature. Ferworn et al. (1993) showed that the formation of asphaltene agglomerates by diluting crude oils with *n*-heptane takes place almost instantaneously.

Effect of Temperature. An increase in temperature affects the agglomeration of asphaltenes by decreasing the solvating power of the crude oil. As a result, the less-soluble, higher molar mass asphaltenes are precipitated initially followed by progressively lighter asphaltene molecules. The subsequent addition of the lower molar mass asphaltenes results in a decrease in the overall molar mass of the precipitated particles (Burke et al., 1990; Hirschberg et al., 1984; Mansoori and Jiang, 1985; Moschopedis et al., 1976).

Effect of Pressure. Burke et al. (1979) and Hirschberg et al. (1984) investigated the effects of pressure on asphaltene precipitation. For oils above their bubble point pressure, increasing the pressure has a positive influence on the solubility parameter. As a result, asphaltenes are generally more soluble in hydrocarbons at higher pressures.

Experimental Apparatus and Procedure

A schematic of the experimental apparatus used for collecting the data reported here is shown as Figure 2. The centerpiece of the apparatus is a Brinkmann 2010 particle size analyzer, which directly measures the particle size by sweeping a laser beam at a known velocity through a cell

containing the sample onto a photocell. By monitoring the interruption of the laser beam by suspended particles, the particle size analyzer combines the results of a large number of such measurements as a size distribution histogram (Ferworn et al., 1993; LeBlanc, 1988). As explained later, modifications were made to the Brinkmann particle size analyzer to allow measurement of particle sizes over the 10–1200- μm range (Nielsen, 1993).

Laser Sampling Cell. A new high-pressure sample cell was designed to replace the originally-supplied microflow cell, as used by Ferworn et al. (1993), which was capable of operation only at atmospheric pressure and ambient temperature. The new laser cell was designed and built to withstand pressures up to 6 MPa at temperatures from 0 to 150 °C. The cell windows were constructed from optical-quality quartz to withstand high-pressure and let the laser beam through uninhibited. The cell was provided with an internal heat exchanger to allow good temperature regulation.

Ancillary Equipment. The high-pressure mixing equipment consisted of two high-pressure cells: a 600-mL cell (H) for mixing the diluent–crude oil mixture and another 16-mL cell (A) for holding the crude oil sample. A centrifugal pump circulated glycol solution to maintain the laser cell at the test temperature. Two pressure gauges were used to monitor the pressure of the main cell (H) and at the discharge of a Gilson 303 pump. The Gilson pump was used to maintain the system pressure and force the diluent–oil mixture through the laser cell. A 500-cm³ Jeffri pump was used to fill the mixing cell with the diluent and inject crude oil samples.

The mixing of crude oil and diluent took place in the stirred high-pressure cell. An air motor, coupled through a planetary gearbox to the stirrer, provided the power for stirring at a constant speed of 150 rev/min. The stirring speed was maintained the same in all experiments to minimize any effect, if any, of changes in the flow regime on the size of asphaltene agglomerates. Diluent was injected into the cell by use of the Jeffri pump. The Gilson pump supplied a monitored rate of hydraulic fluid to the underside of the piston in the main pressure cell, forcing the diluent–oil mixture through the laser cell and back-pressure valves to the waste reservoir. Back pressure was maintained through a series of relief valves that allowed both the addition of the diluent under pressure and the circulation of the mixture during pumping. The crude oil was injected by opening a valve leading to the crude oil storage cell from the Jeffri pump and closing another valve to bypass the main flow line.

Procedure. Before an experiment was started with a new sample, the high-pressure cell (H) was dismantled and the upper chamber was cleaned alternately with toluene and *n*-pentane. The cell was then reassembled and flushed with nitrogen to expel air and other vapors, followed by drawing vacuum to remove the nitrogen. The Jeffri pump was used to measure 250 mL of *n*-pentane into the main pressure cell and to bring the system up to the test pressure.

In a typical experiment, 4.2 mL of crude oil sample was measured and poured into the high-pressure sample cell (A), the air was expelled, and the cell was reconnected to the flow line. A difficulty was encountered while the high-viscosity Cold Lake and Lindberg oils were poured into the high-pressure sample cell (A); hence, these two crude oils were diluted with an equal volume of pure toluene. The low-viscosity Countess oil and Border condensate were poured “as is”, i.e., without any dilution.

After allowing 30 min for the temperature to equalize (with stirring), the contents of the sample cell were forced

Table 1. Analysis of Crude Oil Samples

petroleum sample	asphaltene (pentane-insoluble) content (mass %)	density at 15 °C (kg/m ³)	molar mass (kg/kmol)
Border condensate	0.6	740.8	114
Countess crude oil			
this study	5.7	886.3	251
Ferworn et al. (1993)	8.1	911.0	354
Lindberg heavy oil	17.6	988.0	483
Cold Lake bitumen			
this study	21.8	996.8	522
Ferworn et al. (1993)	16.7	995.0	585

slowly into the high-pressure cell (H) using the Jeffri pump. The Gilson pump was then started to maintain a pumping rate of 1.5–3 mL/min, and the particle size measurement was commenced. A total of 425 runs (including repeated trials) were made using the above procedure with the four oil samples at the selected pressures and temperatures.

Representation of Particle Size Distribution. Ferworn et al. (1993) and Popplewell et al. (1989) suggested that particle size distributions could be modeled using a log-normal curve. The volume-basis probability function, $p(x)$, for the log-normal distribution is given as

$$p(x) = \frac{1}{(2\pi)^{1/2} \sigma x \ln(10)} \exp \left[-\frac{1}{2} \left(\frac{\log x - \log \xi}{\sigma} \right)^2 \right] \quad (1)$$

where $\log \xi$ denotes the mean of $\log(x)$, σ the standard deviation of $\log(x)$, and x the diameter of the asphaltene particle.

In certain processes, particle size distributions can be bimodal, especially when the process involves agglomeration or shattering of particles (Popplewell et al., 1989). A bimodal distribution is modeled using the sum of two weighted log-normal curves:

$$p(x) = \frac{1}{(2\pi)^{1/2} x \ln(10)} \left(\frac{m}{\sigma_1} \exp \left[-\frac{1}{2} \left(\frac{\log x - \log \xi_1}{\sigma_1} \right)^2 \right] + \frac{1-m}{\sigma_2} \exp \left[-\frac{1}{2} \left(\frac{\log x - \log \xi_2}{\sigma_2} \right)^2 \right] \right) \quad (2)$$

where m and $(1-m)$ are the weights of the first and second log-normal curves.

The mean log particle diameter, $\log \xi$, is converted into the mean particle diameter, \bar{d}_p (in μm), by

$$\bar{d}_p = 10^{\log \xi + 1.1513\sigma^2} \quad (3)$$

In eq 3, the mean particle diameter, \bar{d}_p , is seen to be a nonlinear function of the mean and the standard deviation of $\log(x)$. The shift in the mean particle diameter caused by the variance in the standard deviation can mask any change in \bar{d}_p . To avoid this, $\log \xi$ is used to represent the mean particle diameter for most of the results presented in this paper.

Crude Oil Samples. Table 1 lists the molar mass, the density, and the (pentane-insoluble) asphaltene content of the four crude oil samples, ranging from the light asphaltic Border condensate to the heavy and viscous Cold Lake bitumen. Also given in Table 1, for comparison, are analyses for the Countess oil and Cold Lake bitumen samples used by Ferworn et al. (1993).

Preliminary Experiments with Cold Lake Bitumen and *n*-Heptane. A series of experiments were performed by alternating between the original Brinkmann laser cell and the high-pressure laser cell at ambient pressure and temperature to reproduce the results reported by Ferworn et al. (1993). The mean asphaltene particle sizes, with a 1:40 ratio (by volume) of Cold Lake bitumen and *n*-

Table 2. Mean Asphaltene Particle Size Data for Cold Lake Bitumen and *n*-Heptane in 1:60 Ratio at Atmospheric Pressure

temp (°C)	no. of trials	mean \bar{d}_p (μm)	min \bar{d}_p (μm)	max \bar{d}_p (μm)
0	42	287 \pm 69	259	380
50	46	287 \pm 69	243	339

Table 3. Summary of High-Pressure Experiments with *n*-Pentane at 1:60 Dilution Ratio and Results Obtained

petroleum sample	temp (°C)	press. (MPa)	no. of trials		asphaltene particle size statistics			
			total	ignored	$\log \xi$	σ	\bar{d}_p (μm)	
Border condensate	0	2.2	23	1	2.59	0.23	448	
	50	2.2	40	3	2.28	0.47	338	
	100	2.2	35	1	2.36	0.23	266	
Countess oil	0	5.6	21	0	2.60	0.22	450	
	0	2.2	21	4	2.53	0.31	440	
	50	2.2	29	1	2.55	0.29	447	
Lindberg heavy oil	100	2.2	43	0	2.51	0.21	366	
	0	5.6	31	3	2.56	0.33	483	
	0	2.2	32	4	2.60	0.29	495	
Cold Lake bitumen	50	2.2	29	0	2.55	0.25	422	
	0	5.6	34	1	2.59	0.26	457	
	0	2.2	20	2	2.53	0.23	394	
	50	2.2	33	2	2.56	0.29	423	
	0	5.6	33	1	2.53	0.28	444	

heptane, ranged from 254 to 303 μm , which compare favorably with $\bar{d}_p = 286 \pm 82 \mu\text{m}$ reported by Ferworn et al. (1993).

In preliminary experiments at ambient conditions, a high-speed video camera was used to visually examine the shape of asphaltene particles. It was noted that the particles were not round, but instead elongated and irregular in shape (Ferworn, 1992; Nielsen, 1993).

Additional atmospheric pressure experiments were performed at 0 and 50 °C using Cold Lake bitumen diluted with *n*-heptane in a ratio of 1:60. As summarized in Table 2, the results of these 88 repeated experiments showed no effect of temperature between 0 and 50 °C. These experiments confirmed that a large number of repeated trials are necessary to generate statistically significant results. It also became apparent that the particle size range was outside the existing capacity of the Brinkmann analyzer (0–600 μm); hence, modifications were made to expand the range to 10–1200 μm .

Results Obtained at High Pressures with *n*-Pentane

The first set of high-pressure experiments, with *n*-pentane as the diluent, were performed at 0 °C and 5.6 MPa for each crude oil. Subsequently, tests were performed at 2.2 MPa at temperatures of 0, 50, and 100 °C. Results of all high-pressure experiments are summarized in Table 3. Additional experiments were carried out at temperatures higher than 100 °C, but certain difficulties were encountered in measuring the asphaltene particle size. Nonetheless, these higher temperature experiments provided some important insight into asphaltene agglomeration process.

Results at 5.6 MPa. Figure 3 presents the results of experiments with the four crude oils at 0 °C and 5.6 MPa. Aside from a few exceptions, most trials yielded particle size distributions that had similar shapes. Although the precise reason why the trends from a few trials did not conform to a vast majority of the experiments is not clear, these were attributed to partial blockage of flow lines and/or the laser cell by asphaltene particles. In calculating the averages for all of the tests at each set of conditions,

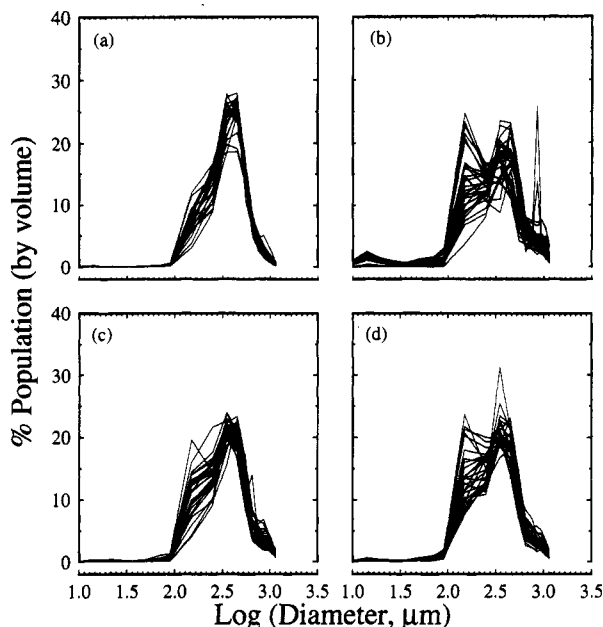


Figure 3. Results of asphaltene particle size analyses at 0 °C and 5.6 MPa: (a) Border condensate, (b) Countess oil, (c) Lindberg oil, (d) Cold Lake bitumen.

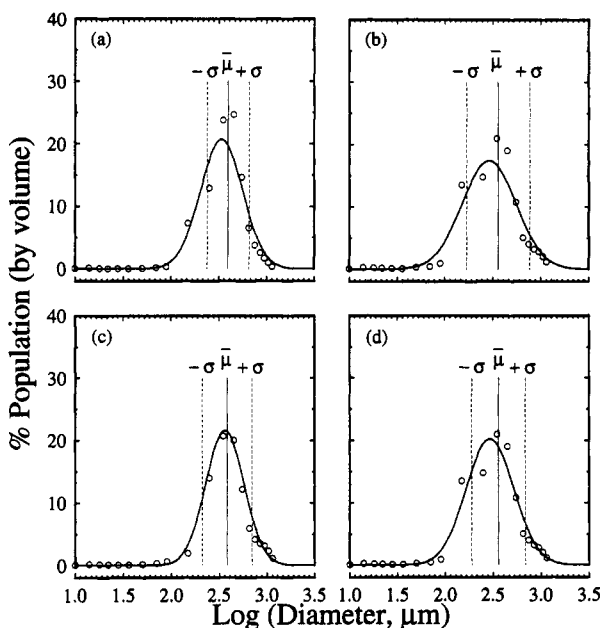


Figure 4. Representation of asphaltene particle size averages at 0 °C and 5.6 MPa with unimodal log-normal function: (a) Border condensate, (b) Countess oil, (c) Lindberg oil, (d) Cold Lake bitumen.

the data for the unusual trials were ignored. The number of trials ignored in calculating the averages are identified in Table 3.

The averages of the experimental data are plotted in Figure 4. Also plotted in Figure 4 are the log-normal curves that were obtained by fitting the data through the minimization of the sum of the square of the errors. The statistical parameters for each curve are also listed in Table 3. It is pointed out that the means ($\bar{\mu}$) shown in Figure 4 were calculated from experimental data and not from the log-normal curve (eq 1).

Results at 2.2 MPa. Figures 5–7 present the results of experiments at 2.2 MPa that were performed at 0, 50, and 100 °C, respectively. Notice that some of the results exhibit more than one particle size distribution, which is not unexpected as agglomeration processes can produce bimodal particle size distributions (Popplewell et al., 1989).

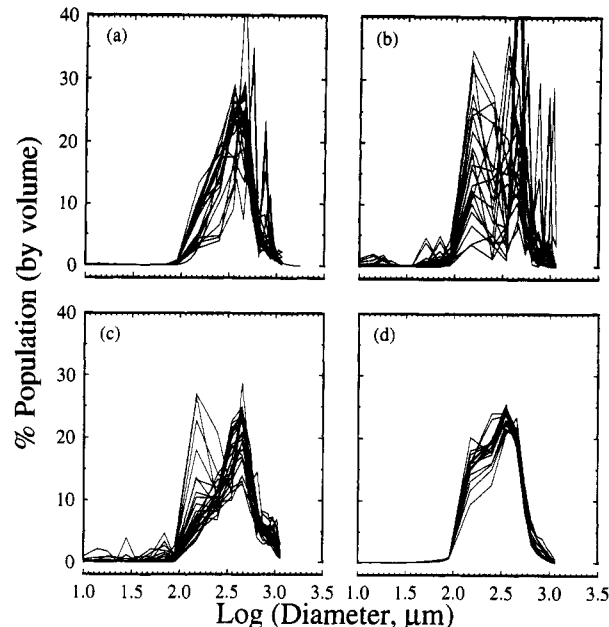


Figure 5. Results of asphaltene particle size analyses at 0 °C and 2.2 MPa: (a) Border condensate, (b) Countess oil, (c) Lindberg oil, (d) Cold Lake bitumen.

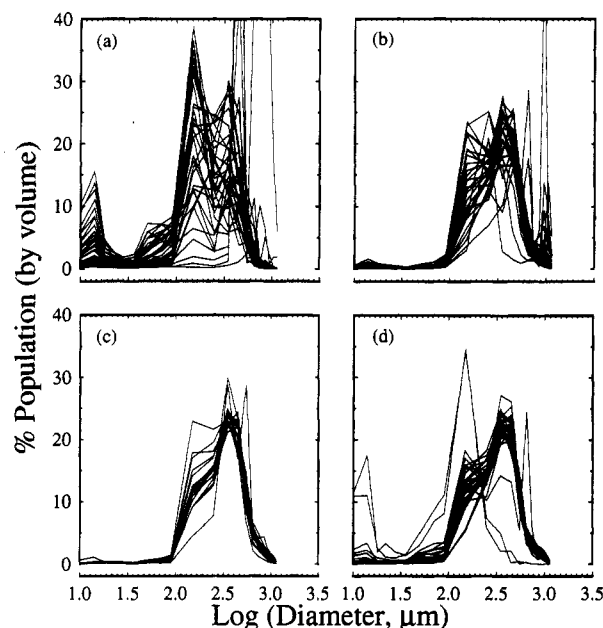


Figure 6. Results of asphaltene particle size analyses at 50 °C and 2.2 MPa: (a) Border condensate, (b) Countess oil, (c) Lindberg oil, (d) Cold Lake bitumen.

Figures 8–10 show the averages of the data shown in Figures 5–7 for all crude oil samples at temperatures of 0, 50, and 100 °C, respectively. The corresponding log-normal curves are also shown in these figures, which in most cases describe the experimental data fairly well.

Experiments at Temperatures Higher Than 100 °C. In experiments with Cold Lake bitumen and Lindberg oil at temperatures higher than 50 °C, asphaltene particles were observed in the laser cell window initially when the crude oil was injected into *n*-pentane. Within a period of 1–3 min, however, the particles disappeared and only clear liquid was seen in the laser cell window. At first, this was attributed to either plugging of the flow lines or, as suggested by Corbett and Petrossi (1975), the formation of another liquid phase. On examining the mixing cell after cooling, it became apparent that the asphaltene

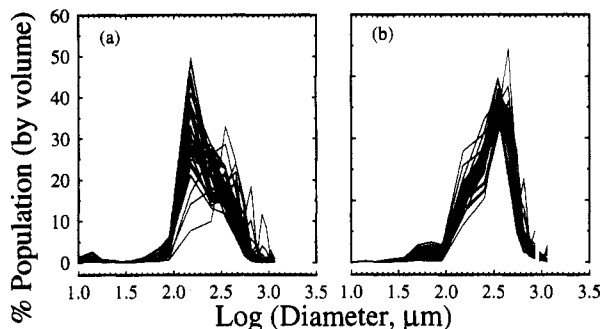


Figure 7. Results of asphaltene particle size analyses at 100 °C and 2.2 MPa: (a) Border condensate, (b) Countess oil.

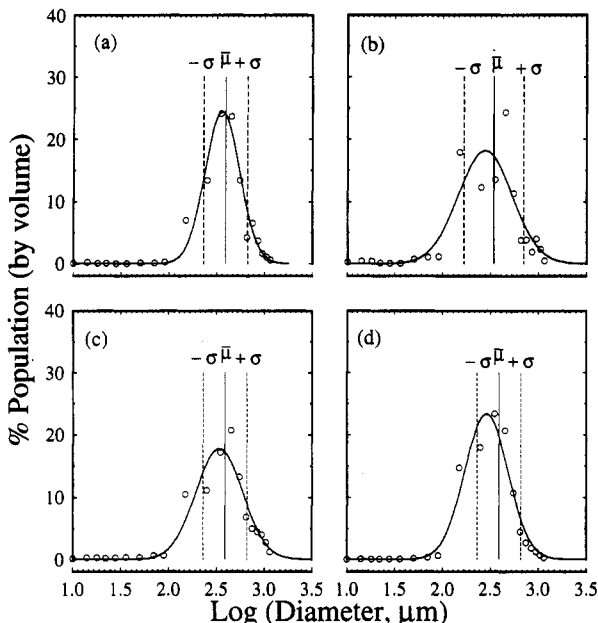


Figure 8. Representation of asphaltene particle size averages at 0 °C and 2.2 MPa with unimodal log-normal function: (a) Border condensate, (b) Countess oil, (c) Lindberg oil, (d) Cold Lake bitumen.

particles had formed 5–10-mm-diameter “super agglomerates”, in a cone-shaped aggregate under the stirrer and scattered across the piston. Experiments with Cold Lake bitumen and Lindberg oil, at temperatures higher than 100 °C, needed to be terminated due to seizing of the piston ring with “gumlike” material. Similar observations with these two crude oils were made even at 75 °C; hence, as shown in Table 3, the highest temperature for data with these heavier crude oils was 50 °C.

Discussion of Results

The asphaltene particle size distribution has been suggested to follow a log-normal distribution (Ferworn et al., 1993), and this is supported by most of the results presented in Figures 4 and 8–10. Listed in Table 4 are the coefficients of multiple determination or the correlation coefficients (r^2) for eq 1, for the trials presented in Table 3. Evidently, a satisfactory representation of all cases is obtained ($r^2 \geq 0.9$), except for Border condensate at 50 °C (Figure 6a or 9a) and Countess oil at 0 °C (Figure 5b or 8b). For these two cases, the asphaltene particle size data clearly exhibit a bimodal distribution, which may reflect the heterogeneous nature of asphaltene micelles in these two crude oils. The data for these two cases were fitted to eq 2, which, as mentioned previously, is a function composed of two log-normal distributions coupled with weights (m) and $(1 - m)$. An optimum bimodal curve for

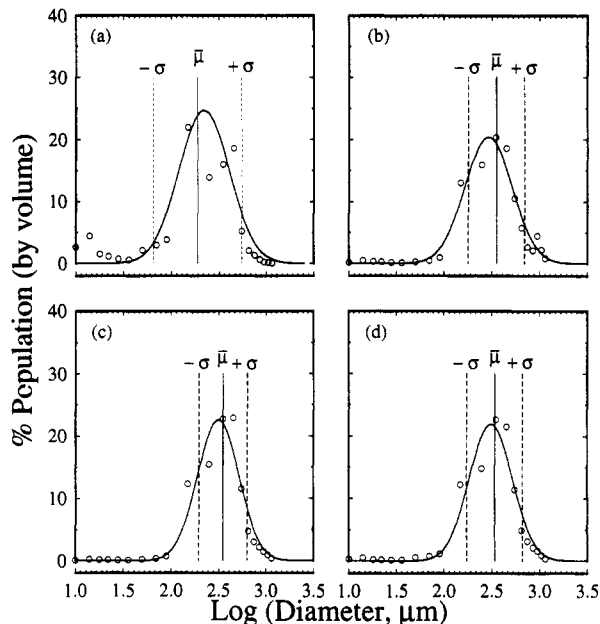


Figure 9. Representation of asphaltene particle size averages at 50 °C and 2.2 MPa with unimodal log-normal function: (a) Border condensate, (b) Countess oil, (c) Lindberg oil, (d) Cold Lake bitumen.

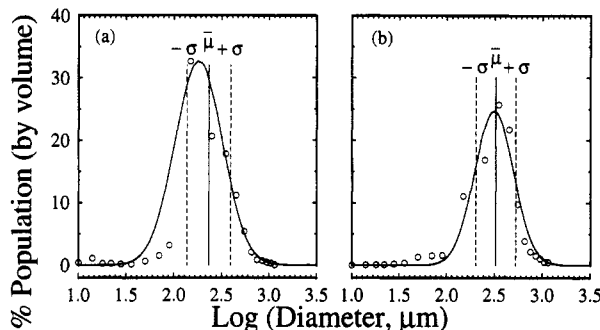


Figure 10. Representation of asphaltene particle size averages at 100 °C and 2.2 MPa with unimodal log-normal function: (a) Border condensate, (b) Countess oil.

Table 4. Coefficient of Multiple Determination for Log-Normal Distribution (Eq 1)

petroleum sample	coeff of mult determination (r^2) at T - P conditions			
	0 °C/ 2.2 MPa	0 °C/ 5.6 MPa	50 °C/ 2.2 MPa	100 °C/ 2.2 MPa
Border condensate	0.95	0.96	0.79	0.91
Countess oil	0.75	0.91	0.94	0.93
Lindberg heavy oil	0.90	0.90	0.92	
Cold Lake bitumen	0.94	0.91	0.92	

each case is shown in Figure 11. The parameters in eq 2 for Figure 11a are $m = 0.43$, $\log \xi_1 = 2.28$, $\log \xi_2 = 2.66$, $\sigma_1 = 0.11$, and $\sigma_2 = 0.16$, and for Figure 11b are $m = 0.35$, $\log \xi_1 = 2.28$, $\log \xi_2 = 2.66$, $\sigma_1 = 0.09$, and $\sigma_2 = 0.11$.

Although bimodal distributions are readily apparent for the two sets of results, they could exist for other results as well. Popplewell et al. (1989) argued that if the means are in close proximity and the standard deviations are relatively large (as is the case for most of the results here), then a bimodal distribution may actually resemble a unimodal distribution. An examination of Figure 5c or 8c, for example, suggests the likelihood of more than one distribution.

Effects of Pressure and Temperature. A dependence of particle size on pressure was expected as the solubility parameter increases with increasing pressure (Hirschberg et al., 1984). Indeed, Figure 12a displays a

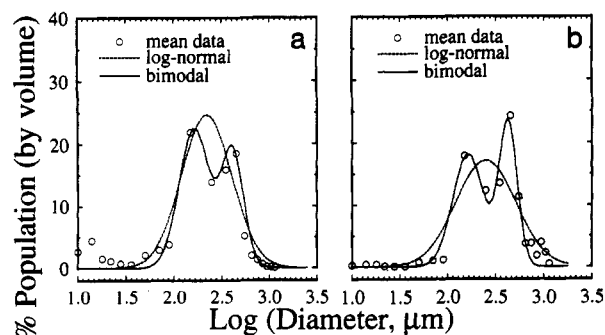


Figure 11. Comparison of unimodal and bimodal log-normal functions fitted to asphaltene particle size averages: (a) Countess oil at 0 °C and 2.2 MPa, (b) Border condensate at 50 °C and 2.2 MPa.

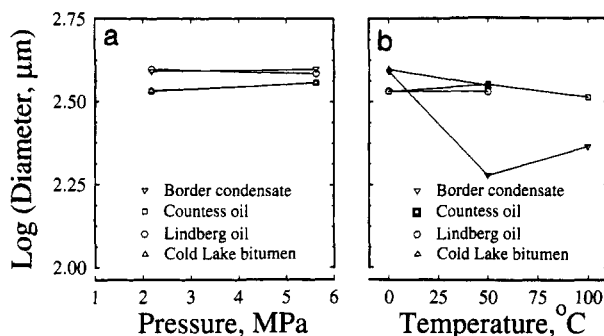


Figure 12. Effects of pressure and temperature on mean asphaltene particle size: (a) at a constant temperature of 0 °C, (b) at a constant pressure of 2.2 MPa.

slight increase in the mean particle size with pressure for all crude oils except the Lindberg oil.

Figure 12b presents the mean particle sizes as a function of temperature for all crude oils. The Border condensate showed an interesting effect of temperature; there is a significant decrease in $\log \xi$ from 2.60 to 2.28 between 0 and 50 °C followed by an increase to 2.36 at 100 °C. The results are similar to those reported for Qaiyarah oil by Ali and Al-Ghannam (1981). It is possible that the asphaltene particles at 0 °C have a greater occlusion of the diluent and maltenes. The Cold Lake, Countess, and Lindberg oils show only slight change in the mean particle size over the temperature ranges.

At higher temperatures (75–150 °C), it appears that the asphaltenes of the heavier crude oils soften to the point where the agglomeration of larger particles takes place due to increased adhesion. As suggested by Speight (1991), it may be caused by an increase in the amount of near-asphaltene molecules (resins of high molar mass) precipitating due to their decreased solubility. The viscosity measurements by Mehrotra et al. (1989) on the heaviest fraction (cut no. 5) of Cold Lake bitumen, which comprised 49 mass % asphaltenes, indicated a softening temperature of approximately 100 °C for the glasslike solid. Furthermore, the observation of Speight (1991) that a decrease in the solubility parameter would precipitate a "tacky" semisolid residue may explain the "super agglomerates" observed with Cold Lake bitumen and Lindberg oil at higher temperatures. Thus, the term "particle size" may not have any significance for asphaltene agglomerates at temperatures higher than approximately 75–100 °C.

Effect of Crude Oil Molar Mass. Figure 13 shows the effect of oil molar mass on the mean asphaltene particle diameter. The experiments at 50 and 100 °C show discernible trends for an increase in particle size with molar mass of crude oils. There is limited agreement with Ferworn et al. (1993), who had found an increase in asphaltene particle size with crude oil molar mass at

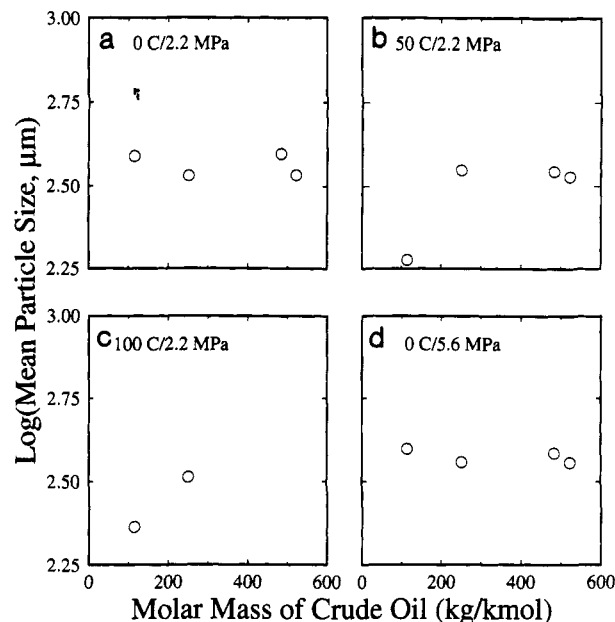


Figure 13. Relationship between molar mass of crude oils and mean asphaltene particle size.

22 °C and atmospheric pressure. However, for other temperature and pressure conditions, i.e., 0 °C and either 2.2 or 5.6 MPa, the results do not show any appreciable dependence of asphaltene particle size with molar mass. Overall, the results of this study suggest a slight increase of the mean asphaltene particle size with an increase in pressure and with a decrease in temperature; however, any effect of crude oil molar mass is not apparent.

Conclusions

Modifications of the Brinkmann particle size analyzer were described for studying the effects of temperature and pressure on the size of asphaltene particles in crude oils diluted with *n*-pentane. Expanding the range for the particle size analyzer to 10–1200 μm proved invaluable to this investigation. Experiments were performed with four crude oil samples diluted (in a volumetric ratio of 1:60) with *n*-pentane at 0–150 °C and up to 5.6 MPa. Although the particle size distribution in most cases was log-normal, the Border condensate and Countess oil showed instances where bimodal distributions were clearly apparent.

An increase in pressure yielded an increase in the mean asphaltene particle size for all oil samples except the Lindberg oil. Varying the temperature from 0 to 100 °C yielded a significant change in the mean particle size for the Border condensate. In experiments with the two higher molar mass crude oils (Cold Lake bitumen and Lindberg oil), "super agglomerates" were observed at temperatures of 75 °C and higher, which is attributed to the softening and adhesion of asphaltene particles.

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Nomenclature

\bar{d}_p = mean particle diameter, μm

m = relative weight of the first log-normal curve

x = diameter of an asphaltene particle, μm

Greek Symbols

$\bar{\mu}$ = mean of particle size analyses, μm

$\log \xi$ = mean of $\log(x)$

σ = standard deviation of $\log(x)$

Subscripts

1 = first log-normal curve in a bimodal distribution

2 = second log-normal curve in a bimodal distribution

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