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Sensitivity of Asphaltene Properties to Separation Techniques

H. Alboudwarej, J. Beck, W. Y. Svrcek, and H. W. Yarranton*

Department of Chemical and Petroleum Engineering, The University of Calgary, Calgary, Canada

K. Akbarzadeh

Department of Chemical Engineering, Shiraz University, Shiraz, Iran

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Asphaltene properties vary with separation method and sometimes with individual technique. Factors such as contact time, solvent-to-crude oil ratio, and temperature influence asphaltene precipitation and are somewhat standardized. However, the final step in most separations, washing the asphaltene filter cake with solvent, is not standardized. Asphaltene properties can be very sensitive to small amounts of resins and therefore may be sensitive to the amount of washing. Asphaltenes were extracted with three different levels of washing from four source oils (Athabasca, Cold Lake, Lloydminster, and Peace River). In all cases, increased washing decreased asphaltene yield and slightly increased asphaltene density. Increased washing significantly increased molar mass and decreased the solubility of the extracted asphaltenes. A new washing method using a Soxhlet apparatus removed the largest amount of resinous material and yielded asphaltenes with significantly different properties from conventionally washed asphaltenes. Since more resinous material was removed, the Soxhlet method allows a more direct comparison between asphaltenes from different sources. Asphaltenes were also extracted using three standard separation methods, IP 143, ASTM D4124, and a method proposed by Speight. Some property variations between the methods were observed and a set of criteria to obtain consistent samples is proposed.

Introduction

With the decline of conventional crude oil production, producers have begun to exploit heavy oil reservoirs and offshore fields resulting in increased production problems associated with asphaltene deposition. These asphaltene deposits have the potential to disable production operations anywhere from the oil reservoir to the production lines and storage tanks. To develop effective methods for mitigating asphaltene deposition, it is first necessary to model asphaltene precipitation. Most modeling approaches require measurements of asphaltene properties such as molar mass and density as well as some precipitation data with which to tune the model.

It has proven difficult to achieve consistent asphaltene property measurements because they are a solubility class and not a pure component. Typically, crude oils are separated into four solubility fractions: saturates, aromatics, resins, and asphaltenes (SARA). The saturates generally consist of naphthenes and paraffins. The aromatics, resins, and asphaltenes appear to form a continuum of polynuclear aromatic species of increasing molar mass, polarity, and heteroatom content. There is no clear distinction between asphaltenes and resins. Consequently, the amount of asphaltenes extracted from

a crude oil depends on the type of solvent, dilution ratio, contact time, and temperature.¹

The effect of contact time on the amount of precipitated asphaltenes is shown in Figure 1a. The yield increases over the first few hours reaching a plateau after approximately 24 h. The effect of adding more solvent, i.e., increasing the solvent-to-bitumen ratio, is shown in Figure 1b. The yield increases and reaches a plateau at solvent-to-bitumen ratios above approximately 25 cm³/g. The amount of precipitation depends on the solvent; for example, the precipitation curves in Figure 1 shift upward as the carbon number of an *n*-alkane solvent decreases below seven. The curves shift downward as temperature increases since the solubility of the asphaltenes increase with increasing temperature.²

The importance of solvent, solvent-to-bitumen ratio, contact time, and temperature is well established and standard separation procedures have been developed in an effort to obtain consistent asphaltene fractions. It is general practice to use *n*-pentane to extract asphaltenes if the de-asphalted oil is to be further subdivided by adsorption chromatography into resins, aromatics, and saturates. If higher-carbon-number alkanes are used,

(1) Speight, J. G. *The Chemistry and Technology of Petroleum*, 3rd ed.; Marcel Dekker Inc., New York, 1998.

(2) Speight, J. G.; Long, R. B.; Trowbridge, T. D. *Fuel* **1984**, 63, 616–620.

* Corresponding author. Phone: (403) 220-6529. Fax: (403) 282-3945. E-mail: hyarrant@ucalgary.ca.

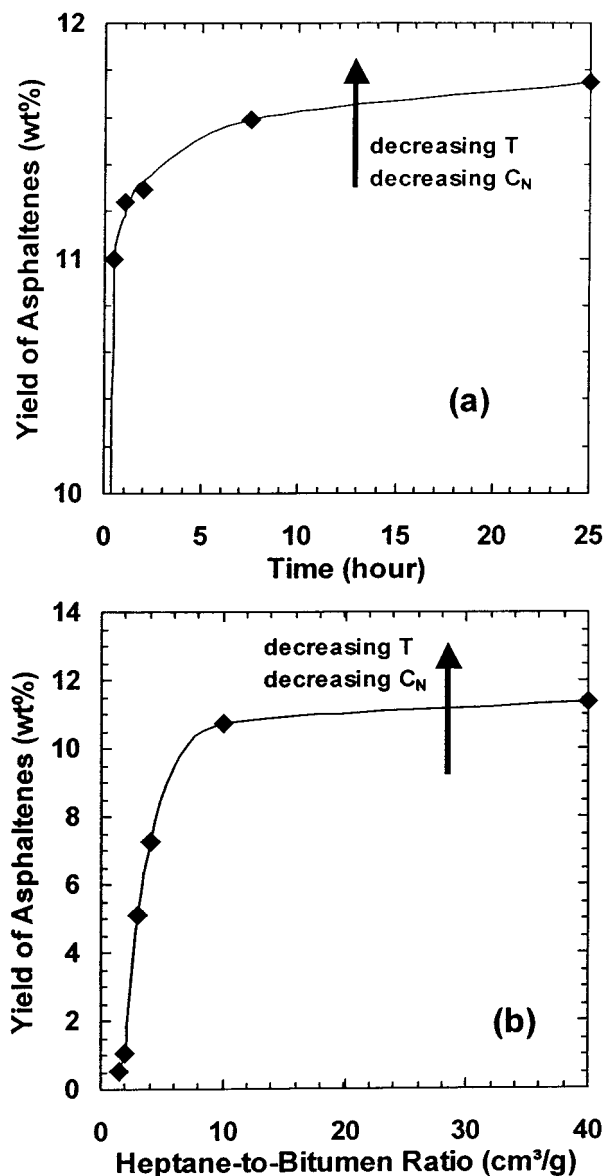


Figure 1. Effect of contact time and heptane-to-bitumen ratio on the asphaltene yield from Athabasca bitumen No. 2 at 23 °C. (a) Contact time at a 40:1 heptane:bitumen ratio; (b) heptane-to-bitumen ratio at 24 h of contact time. (Asphaltenes were centrifuged from bitumen/heptane mixtures at 3500 rpm for six minutes and then sonicator washed.)

less asphaltenes are separated and significant amounts of residual "asphaltenic resins" adsorb permanently on the chromatographic column. *n*-Heptane is commonly used as the separating solvent for asphaltene studies because asphaltene properties do not vary significantly with the carbon number of the solvent for *n*-heptane and higher-carbon-number alkanes.³ A solvent-to-bitumen ratio of 40 cm³/g is used for most separation methods and the recommended contact time is 12–16 h for *n*-pentane separation and overnight (16–24 h) for *n*-heptane separation. In most cases, separations are carried out at ambient conditions for convenience.

In most methods, the precipitated asphaltenes are filtered from the solvent–crude oil mixture. The filter cake is washed with solvent to remove resinous materials. The asphaltenes are then dried and recovered. Most

experimental methods available do not precisely indicate how much washing is necessary. For example, one common criterion is that washing should continue until the effluent from the filter cake is colorless.⁴ Another criterion is that washing should continue until evaporation of a few drops of the effluent does not leave any residue on a glass slide.⁵ These criteria are imprecise and it is almost certain that different individuals will obtain asphaltenes with different amounts of washing. For many substances these small differences would not be expected to significantly affect their measured properties. However, recent work has demonstrated that even small amounts of resinous material can significantly alter measured asphaltene properties such as molar mass and solubility.^{6,7} Therefore, the level of washing may be a much more critical part of the separation procedure than previously anticipated.

The aim of this paper is to examine the effect of different degrees of washing on the asphaltene properties that are used in the modeling of asphaltene phase behavior; that is, molar mass and density. The effect of washing on measured asphaltene solubility is also examined. Properties of asphaltenes from several crude oils are compared after different levels of washing. In addition, the properties of asphaltenes extracted using three different "standard" techniques are compared with a proposed new separation method.

Experimental Section

Materials and Chemicals. Athabasca and Cold Lake bitumens were obtained from Syncrude Canada Ltd., Lloydminster heavy oil was obtained from Husky Oil Ltd., and Peace River heavy oil was obtained from Amoco Canada Petroleum Company Ltd. The Athabasca bitumen was an oil-sand bitumen that had been processed to remove sand and water. Two different Athabasca bitumen samples were obtained. The first sample is referred to as Athabasca bitumen and the second one as Athabasca bitumen No. 2. The Cold Lake and Peace River samples were recovered by steam injection from an underground reservoir and had also been processed to remove sand and water. The Lloydminster heavy oil was a wellhead sample from a cyclic steam injection project and had not been processed.

Both the Lloydminster and Peace River samples contained water, which was removed by diluting the oils with *n*-heptane to a ratio of 0.8 cm³/g. At this ratio, the density of the oil was reduced sufficiently for the water to settle. The supernatant was decanted and the *n*-heptane was removed in a rotary evaporator at 70 °C and 485 mmHg vacuum. The water content of the treated heavy oil was measured using Karl Fischer titration and was found to be less than 2 wt % in both cases. *n*-Heptane was used to remove the water from bitumen since it causes water droplets to flocculate and settle more readily. Also, it is possible that toluene may alter the association state of the asphaltenes in the bitumen and affect the yield and properties of the separated asphaltenes. This is not an issue with *n*-heptane since it is added to the bitumen/heavy oil in any case to separate the asphaltenes. We did compare the water content of the oils treated with *n*-heptane or toluene

(4) Annual Book of ASTM Standards, American Society of Testing and Materials, Standard No. D4124-97.

(5) Asphaltene (*n*-heptane insolubles) in petroleum products, Standards for petroleum and its products, Standard No. IP 143/90, Institute of Petroleum, London, U.K., 143.1–143.7, 1985.

(6) Alboudwarej, H.; Akbarzadeh, K.; Svrcek, W. Y.; Yarranton, H. W. Paper #2001-63, Can. Int. Pet. Conf., Calgary, June 12–14, 2001.

(7) Agrawala, M.; Yarranton, H. W. *Ind. Eng. Chem. Res.* **2001**, *40*, 4664–4672.

for water removal and the results were very similar. Toluene and *n*-heptane were obtained from Omnisolv (supplied by VWR Canlab Canada) and were greater than 99.9% pure. Whatman #2 filter paper (8 μ m pore size) was used for all filtrations.

Asphaltene Separation. Four separation procedures were used: ASTM D4124,⁴ IP 143,⁵ Speight method,¹ and a proposed new "Soxhlet method". IP 143 and ASTM D4124 are the most commonly used standard methods for the separation of asphaltenes from crude oils and details of these procedures are not repeated here. However, it should be noted that in the washing step of ASTM D4124 method, we used the Soxhlet apparatus for cleaning the asphaltenes, although only washing with hot *n*-heptane is mentioned in the procedure. The Speight procedure is included because his group has generated a considerable amount of property data on asphaltenes.^{1,2,8} The Speight method includes the following separation steps: [1] add 30 cm³ of *n*-heptane per gram of crude oil, [2] allow 8–10 h of settling, and [3] filter the precipitated asphaltenes. After separation, the asphaltenes are dispersed in toluene (10 cm³ of toluene for each gram of asphaltene) to remove adsorbed resins. Asphaltenes are then reprecipitated with *n*-heptane at a 50:1 volume ratio of *n*-heptane to toluene solution. Speight recommended repeating the later step three times to make sure all the resins were desorbed from the asphaltenes.

A new asphaltene separation method was also tested. The proposed method is intended to maximize the removal of resins and to eliminate the vagaries of the washing step. *n*-Heptane was added to the crude oil at a 40:1 (cm³/g) ratio. The mixture was sonicated for 45 min at room temperature. For more viscous samples such as Athabasca and Cold Lake bitumens, the mixture was initially mixed with a spatula to enhance bitumen–solvent contact. The mixture was left to equilibrate for 24 h. After settling, the supernatant was filtered without disturbing the whole solution. At this point approximately 10% of the original mixture remained unfiltered. Additional *n*-heptane was added to this solution at a 4:1 (cm³/g) ratio of *n*-heptane to the original bitumen mass. The mixture was sonicated for 30 min and left overnight. The mixture was then filtered using the same filter paper. The 2-stage heptane addition results in a significantly less sticky filter cake than a single-stage heptane addition.

The asphaltenes retained on the filter paper at this point are considered to be "Unwashed" asphaltenes. Three degrees of additional washing were also examined yielding "Filter-washed", "Sonicator-washed", and "Soxhlet-washed" samples.

- **Filter-washed asphaltenes:** the Unwashed sample was washed on the filter paper with *n*-heptane. The washing continued for 5 days after which the effluent color was almost colorless.

- **Sonicator-washed asphaltenes:** the Filter-washed sample was transferred to a beaker with *n*-heptane at a ratio of 40:1 cm³/g *n*-heptane to original bitumen. The mixture was sonicated for 30 min and allowed to settle for 1 h. The supernatant was decanted and filtered. The precipitate remaining in the beaker was combined with another 40:1 ratio of *n*-heptane and the same procedure repeated 5–6 times over 5 days. The sonicator dispersed the asphaltene exposing more surface area and allowing greater removal of resinous material. The final supernatant was colorless.

- **Soxhlet-washed asphaltenes:** the Sonicator-washed sample was placed in a Soxhlet apparatus and refluxed with *n*-heptane for 2 days. The heating rate, condenser cooling rate, and fluid level of the solvent in the Soxhlet apparatus were adjusted to maintain a temperature of 30 \pm 3 $^{\circ}$ C in the sample chamber. To improve contact between the asphaltenes and the *n*-heptane, the Soxhlet procedure was interrupted at least once a day and the asphaltene sample was crushed and mixed. A Soxhlet-washed asphaltene sample could also be prepared by

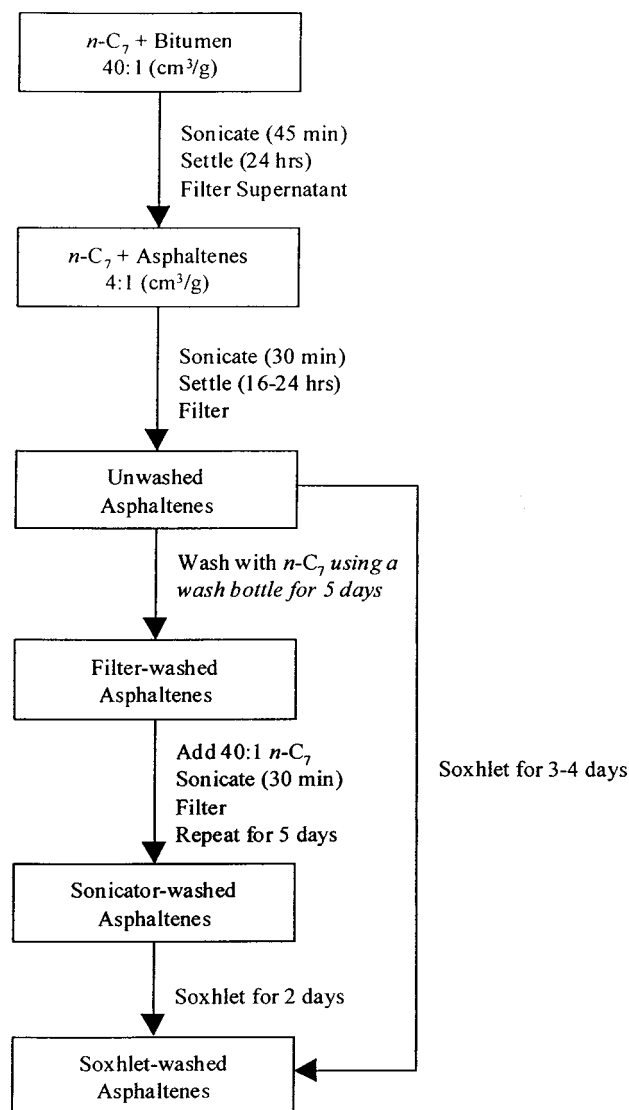


Figure 2. Schematic representation of extraction of different degree washed asphaltenes.

applying the Soxhlet procedure directly to Unwashed asphaltenes for at least 3 days.

The washing procedures are summarized in Figure 2.

Asphaltenes were dried under air prior to the characterization experiments. It is known that asphaltenes oxidize at very high temperatures or if exposed to air for extended period of time at low temperatures.⁹ To examine the effect of any potential oxidation, the asphaltenes were dried both under air and nitrogen. The solubility of the asphaltenes was the same after either air-drying or nitrogen-drying as shown in Figure 3. Since solubility is sensitive to the asphaltene molar mass, the molar masses almost certainly have not been affected. The drying experiments do not prove that oxidation has not occurred. However, they do demonstrate that whatever oxidation may have occurred while drying has not significantly affected the asphaltene properties of interest.

Removal of Non-Asphaltene Solids. Non-asphaltene solids (here referred to as "solids") coprecipitate with asphaltenes.⁸ However, solids-free asphaltenes are required for molar mass and density measurements. To obtain solids-free asphaltenes, asphaltene samples were dissolved in toluene at a 50:1 cm³/g ratio, sonicated for 1 h, and left overnight allowing the solids to settle. The solution was then filtered. Toluene

(8) Mitchel, D. L.; Speight, J. G. *Fuel* **1973**, 52, 149–152.

(9) Moschopedis, S. E.; Parkash, S.; Speight, J. G. *Fuel* **1978**, 57, 431–434.

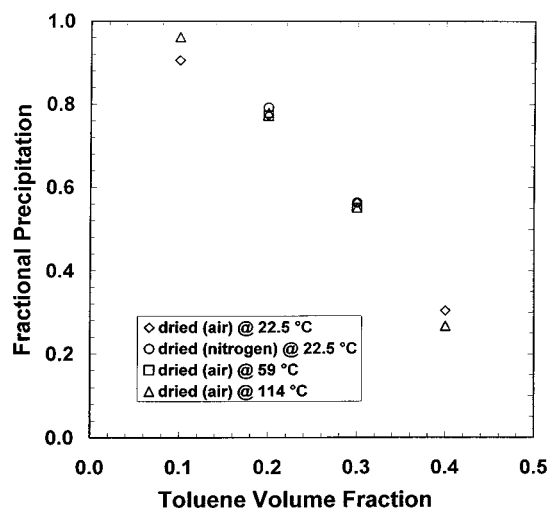


Figure 3. Solubility of Athabasca asphaltenes dried under different conditions.

was evaporated from the solution first in air at room temperature for 2–3 days and then in a vacuum oven under nitrogen at 70 °C. Typically, no further change in mass was observed after 2 days in the oven. However, these samples still contain fine solids that pass through the filter, but the quantity of fine solids was assumed to be too small to influence the property measurements.

A precipitation method was developed to measure the non-asphaltenic solids content of the asphaltenes. Experimental results show that virtually all of the solids appear to coprecipitate with the first asphaltene to precipitate. Therefore, solid content can be measured by precipitating a small fraction of the asphaltenes (plus all of the solids) and then redissolving the asphaltene using toluene. *n*-Heptane was added to a solution of asphaltene-solids in toluene at a 60:40 volume ratio of *n*-heptane to toluene. The sample was centrifuged at 3500 rpm for 6 min. The supernatant was decanted. Fresh toluene was added to dissolve the precipitated asphaltene and then decanted. This procedure was repeated until the toluene solution was colorless. The remaining solids were dried and weighed.

Yield and Property Measurements. Asphaltene yields are reported as the mass of asphaltene (including non-asphaltenic solids) recovered after washing and drying divided by the mass of bitumen/heavy oil. Yields were found to be consistent to $\pm 0.2\%$.

Densities were measured with an Anton Paar DMA 46 density meter calibrated with demineralized water and air. The instrument is accurate to $\pm 0.5 \text{ kg/m}^3$ and all measurements were made at $22.5 \pm 0.05 \text{ }^\circ\text{C}$. Asphaltene densities were calculated indirectly from the densities of mixtures of asphaltene in toluene as described elsewhere.¹⁰

Molar masses of SARA fractions were determined with a Jupiter instrument model 833 vapor pressure osmometer (VPO) calibrated with sucrose octaacetate. The VPO technique is described elsewhere.¹¹ All molar mass measurements were made in toluene at 50 °C and were accurate to $\pm 15\%$. Asphaltene molar mass depends on composition, temperature and pressure. The measured molar mass typically increases as asphaltene concentration increases until a limiting molar mass is reached. This increase in molar mass has been attributed to asphaltene association.¹¹ The average molar mass decreases in a better solvent and at higher temperatures. Therefore, to compare the molar mass of different asphaltene

Table 1. Effect of Washing on Asphaltene Properties

asphaltene sample	yield ^a (%)	solids ^b (%)	density ^c (kg/m ³)	molar mass ^d (g/mol)
Athabasca				
Unwashed	17.4	6.3	1181	5700
Filter-washed	14.2	7.6	1189	7900
Sonicator-washed	13.9	7.8	1190	7600
Soxhlet-washed	12.7	8.6	1192	9100
Cold Lake				
Unwashed	12.7	2.1	1178	
Filter-washed	11.4	2.3	1182	7600 ^e
Soxhlet-washed	7.2	3.7	1190	10400
Lloydminster				
Filter-washed	13.1	2.8	1177	4900
Soxhlet-washed	10.3	3.6	1181	9500
Peace River				
Filter-washed	15.4	2.1	1180	6300
Soxhlet-washed	12.2	2.6	1182	9100

^a Mass percent of bitumen (with solids). ^b Mass percent of asphaltene. ^c Solid-free asphaltene. ^d Molar mass is at 10 kg/m³. ^e Interpolated.

samples, the molar masses were measured over a range of concentrations.

Asphaltene solubility was determined in solutions of toluene and *n*-heptane at an asphaltene concentration of 10 kg/m³ at room temperature and atmospheric pressure. Asphaltene are soluble in toluene but insoluble in *n*-heptane; hence, the fractional asphaltene precipitation increases from zero to one as the *n*-heptane volume fraction increases from zero to one. A plot of fractional precipitation versus toluene or *n*-heptane volume fraction is referred to as a "solubility curve". Details of the solubility experiments are given elsewhere.¹² Also, all the reported solubility curves are corrected to a solids-free basis. Fractional asphaltene precipitation measurements were accurate to $\pm 5\%$.

Results and Discussion

Effect of Washing on Asphaltene Properties. To determine the effect of washing on asphaltene yield and properties, the yield, molar mass, density, and solubility were compared for Unwashed, Filter-washed, Sonicator-washed, and Soxhlet-washed Athabasca asphaltene. Table 1 shows that, as the level of washing increased, the yield decreased monotonically from 17.4% for Unwashed asphaltene down to 12.7% for Soxhlet-washed asphaltene. There was also a change in the appearance of the asphaltene after washing. The Unwashed asphaltene were black and sticky. Both Filter-washed and Sonicator-washed asphaltene were a black to dark brown powder while the Soxhlet-washed asphaltene were a brown powder.

Increased washing likely removes trapped maltene and relatively high molar mass resins. When asphaltene are first precipitated from a crude oil and collected on a filter paper, they form a layer through which the supernatant drains. As a result, some maltene may become trapped within the structure of the precipitate and some maltene components such as resins may adsorb on the asphaltene precipitate. Washing can strip off these materials. Washing also changes the equilibrium between the precipitated asphaltene and the asphaltene in solution since the original supernatant is replaced with a pure solvent that is infinitely dilute in asphaltene. Since asphaltene consist of many

(10) Yarranton, H. W.; Masliyah, J. H. *AIChE J.* **1996**, *42* (12), 3533–3543.

(11) Yarranton, H. W.; Alboudwarej, H.; Jakher, R. *Ind. Eng. Chem. Res.* **2000**, *39*, 2916–2924.

(12) Mannistu, K. D.; Yarranton, H. W.; Masliyah, J. H. *Energy Fuels* **1997**, *11*, 615–622.

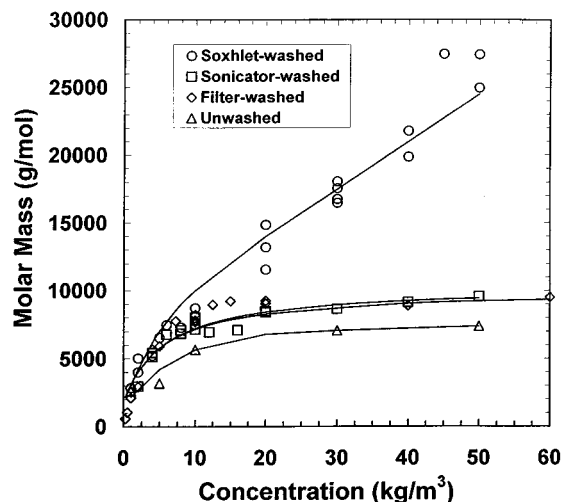


Figure 4. Effect of washing on the molar mass of Athabasca asphaltenes.

thousands of chemical species with a range of solubilities, some of the precipitated asphaltenes will typically redissolve in the pure solvent. These more soluble asphaltenes are likely the smaller more resinous fraction of the asphaltenes. Note that when asphaltenes are fractionated, the properties of the most soluble fraction approach resin properties.¹⁰

The density of the asphaltenes, given in Table 1, increased slightly with increased washing. The increase in density is expected since more washing removes more of the low molar mass, less dense material from the asphaltene samples. Nonetheless, the densities do not change by more than 1%. Therefore, asphaltene densities are not very sensitive to the separation technique.

The molar mass of asphaltenes increased as the degree of washing increased, as shown in Figure 4. As more resinous material is removed, the asphaltenes self-associate to a greater extent and the average molar mass increases. With conventional washing, the molar masses in all cases reached limiting values. However, the molar mass of the Soxhlet-washed asphaltenes increased continuously over the measured concentration range. The extensive washing may have removed virtually all of the resinous material so that the asphaltenes could self-associate without limit as the asphaltene concentration increased. Molar masses at an asphaltene concentration of 10 kg/m³ are given in Table 1. Note that the yield decreased and the density and molar mass increased with increased washing for all of the Western Canadian crude oils, as shown in Table 1.

Asphaltene precipitation depends on the molar mass and density of the asphaltenes. The molar mass in particular is affected by the extent of washing. Therefore, it is of interest to assess the effect of washing on asphaltene precipitation. The solubility curves of Athabasca asphaltenes are shown in Figure 5 at an asphaltene concentration of 10 kg/m³. As the amount of washing increases, the curves shift to the right; that is, more toluene (less *n*-heptane) is required to reach the same amount of precipitation. In other words, the greater the degree of washing, the less soluble the asphaltenes become. The decrease in solubility is likely a result of removing resinous material and the consequent increase in asphaltene self-association. The average molar mass

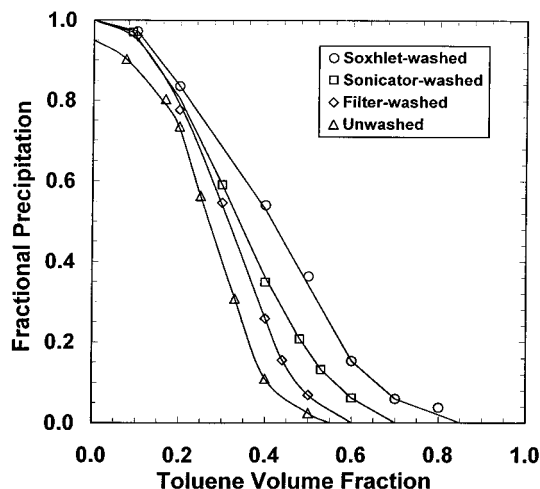


Figure 5. Effect of washing on the solubility of Athabasca asphaltenes in mixtures of toluene and heptane.

of the asphaltenes increases and the higher molar mass material is less soluble. Note that the solubility curves of the Sonicator-washed asphaltenes are different from those of the Filter-washed asphaltenes even though their molar masses were not significantly different. Scatter in the VPO measurements may have obscured differences in the molar mass.

Comparison of Asphaltenes from Different Sources. To develop generalized precipitation models, it is necessary to use data from asphaltenes from different sources/locations. Hence, one question of interest is: how do asphaltenes from different sources compare after different levels of washing? Asphaltene properties from four Western Canadian heavy oils/bitumens were compared to assess the impact of washing.

Asphaltene yields from the four oils are given in Table 1. The Filter-washed asphaltene yields ranged from 11.4% to 15.4% and the Soxhlet-washed asphaltene yields ranged from 7.2% to 12.7%. On average, Soxhlet-washing removed 22% of the Filter-washed asphaltenes. The measured densities fell within a narrow range of 1177 to 1189 kg/m³ and 1181 to 1192 kg/m³ for Filter-washed and Soxhlet-washed asphaltenes, respectively. The densities do not correlate to the yield and likely reflect some chemical differences between asphaltenes from the different sources. The average density increased from 1182 kg/m³ after filter washing to 1186 kg/m³ after Soxhlet washing. Again asphaltene density is not very sensitive to the amount of washing.

The molar masses of Filter-washed asphaltenes from the four heavy oils/bitumens are compared in Figure 6. Molar masses at an asphaltene concentration of 10 kg/m³ are given in Table 1. The two bitumens (Athabasca and Cold Lake) have very similar molar masses at all concentrations. The heavy oils (Peace River and Lloydminster) have lower molar masses than the bitumens at low concentrations and similar molar masses at high concentrations since the heavy oil molar masses continue to increase throughout the concentration range. It was observed that the heavy oil resins were more easily removed than bitumen resins. Therefore, the asphaltene association in Filter-washed samples from the heavy oils may be less inhibited than Filter-washed samples from the bitumens.

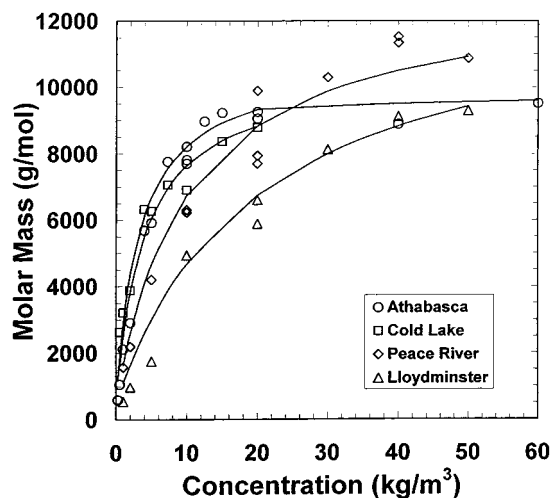


Figure 6. Molar mass of Filter-washed asphaltenes from different sources.

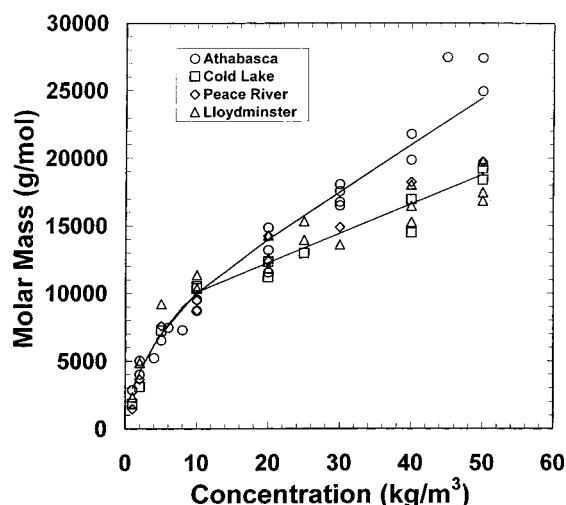


Figure 7. Molar mass of Soxhlet-washed asphaltenes from different sources.

The molar masses of the Soxhlet-washed asphaltenes from different sources are shown in Figure 7. All of the asphaltenes have similar molar mass below concentrations of 10 kg/m³. Above 10 kg/m³, the Athabasca asphaltenes have the highest molar mass. The Cold Lake, Peace River, and Lloydminster asphaltenes fall on the same lower molar mass trend, within the scatter of the data. The Soxhlet washing appears to have removed all of the resinous material from both the bitumens and the heavy oils.

The solubility curves of Filter-washed and Soxhlet-washed asphaltenes from the four source crude oils/bitumens are compared in Figures 8 and 9, respectively. The solubilities correlate to the molar mass although scatter in the VPO data complicates the analysis. The error in the molar masses at an asphaltene concentration of 10 kg/m³ is approximately ± 1000 g/mol. Figure 8 shows that the Filter-washed Athabasca, Cold Lake, and Peace River asphaltenes follow the same solubility trend. Recall from Figure 6 that, at an asphaltene concentration of 10 kg/m³, the molar masses of these samples were similar within the scatter of the data. The Lloydminster asphaltenes, with the lowest molar mass, are more soluble. Figure 9 shows that the Soxhlet-

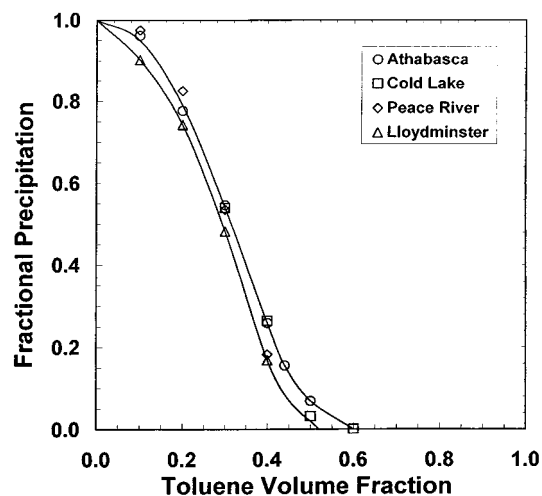


Figure 8. Solubility of Filter-washed asphaltenes from different sources in mixtures of toluene and heptane.

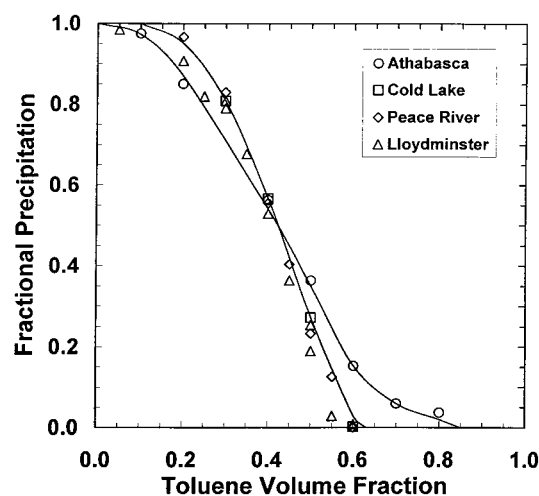


Figure 9. Solubility of Soxhlet-washed asphaltenes from different sources in mixtures of toluene and heptane.

washed Cold Lake, Peace River, and Lloydminster asphaltenes follow the same solubility trend. These samples also followed the same molar mass trend, as was shown in Figure 7. The Soxhlet-washed Athabasca asphaltenes had the highest molar mass trend and the lowest solubility.

It appears that increased washing most affects molar mass. Changes in molar mass in turn affect solubility. Soxhlet-washed samples are less likely to contain resinous material and therefore may provide a more accurate assessment of differences between asphaltenes from different sources.

Comparison of Different Separation Methods.

As pointed out in the Introduction, a number of methods have been used to extract asphaltenes and each method may give asphaltenes with different properties. To assess the impact of the different methods, properties were measured and compared for asphaltenes extracted with four techniques: ASTM D4124, IP 143, Speight Method, and the Soxhlet method. Critical factors in the methods such as contact time, solvent composition, solvent-to-bitumen ratio, temperature, and level of washing are compared in Table 2. Asphaltene yields and densities are given in Table 3. Molar masses and solubility curves are given in Figures 10 and 11,

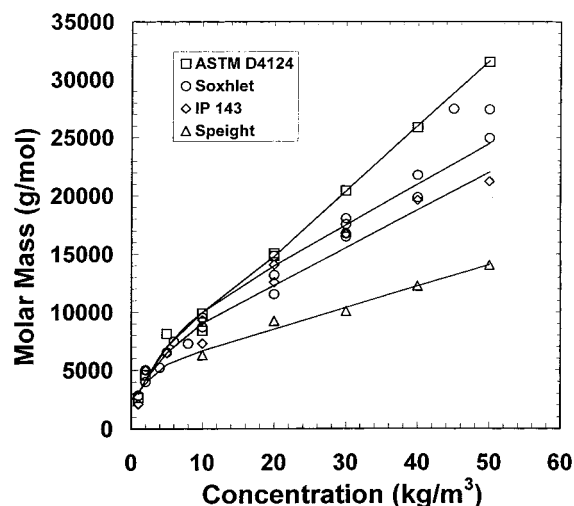
Table 2. Comparison of Asphaltene Extraction Methods

method	solvent addition step	equilibration step	washing step
ASTM D4124	<i>n</i> -heptane: S/B = 100 cm ³ /g, 1 h boiling (98 °C)	24 h at 23 °C	Soxhlet washing at 30 °C for 24 h
IP 143	<i>n</i> -heptane: S/B = 30 cm ³ /g, 1 h boiling (98 °C)	none	Soxhlet washing at 30 °C for 1–2 h
Speight	<i>n</i> -heptane at 23 °C S/B = 30 cm ³ /g	8–10 h at 23 °C	Disperse in toluene and reprecipitate with heptane three times at 23 °C
Soxhlet	(1) <i>n</i> -heptane at 23 °C S/B = 40 cm ³ /g (2) <i>n</i> -heptane at 23 °C S/B = 4 cm ³ /g	24 h at 23 °C for each step	Soxhlet washing at 30 °C for 72 h

Table 3. Effect of Extraction Method on Asphaltene Properties. Asphaltenes Extracted from Athabasca Bitumen No. 2

asphaltene sample	yield ^a (%)	solids ^b (%)	density ^c (kg/m ³)	molar mass ^d (g/mol)
ASTM D4124	9.3	5.7	1215	9200
IP 143	8.7	5.6	1203	8300
Speight	9.2	5.6	1190	6300
Soxhlet	9.8	5.3	1192	9100

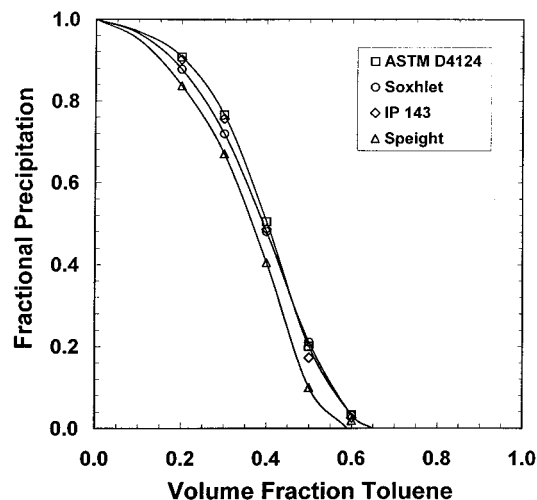
^a Mass percent of bitumen (with solids). ^b Mass percent of asphaltene. ^c Solid-free asphaltene. ^d Molar mass at 10 kg/m³.

**Figure 10.** Effect of extraction method on the molar mass of Athabasca asphaltenes.

respectively. In all cases, the asphaltenes were extracted from Athabasca Bitumen No. 2.

The ASTM D4124, IP 143, and Soxhlet methods provide asphaltenes with similar properties. However, the IP 143 method has a significantly lower yield of asphaltenes. The IP 143 method has a short contact time (1 h) between *n*-heptane and the original heavy oil, which results in smaller amounts of precipitated asphaltenes (see Figure 1a). The Soxhlet method with the longest contact time (36–48 h) has the highest yield. The IP 143 asphaltenes have slightly lower molar mass than the ASTM D4124 and Soxhlet method asphaltenes. The relatively short washing step (1–2 h) in the IP 143 method may not remove as much resinous material.

The Speight method produces asphaltenes with significantly different properties than the other three methods. The asphaltenes extracted with this method have the lowest molar mass and highest solubility. The Speight method also has a lower yield than the ASTM

**Figure 11.** Effect of extraction method on the solubility of Athabasca asphaltenes in mixtures of toluene and heptane.

D4124 and Soxhlet methods. It appears that the Speight method gives more resinous asphaltenes at a relatively low yield. The short contact time (8–10 h) may explain the low yield and the washing step does not appear to remove as much resinous material as the other methods.

Conclusions

The amount of washing is an important consideration in the separation of asphaltenes. As the amount of washing increases, density increases, molar mass increases, and solubility decreases. The change in properties with washing is likely related to asphaltene self-association. Washing removes resinous material and the less resins present, the more the asphaltenes self-associate. Consequently, the average density and molar mass both increase with greater washing. Denser, higher-molar-mass material is less soluble, hence solubility decreases with greater washing.

Conventional washing methods cannot remove all the resinous material. The proposed Soxhlet method removes an additional 10% of the material from Filter-washed asphaltenes. Properties of the Soxhlet-washed asphaltenes are significantly different from conventionally washed asphaltenes. Since more resins are removed, the Soxhlet method allows a more direct comparison of asphaltenes from different sources.

Three "standard" asphaltene separation techniques and the Soxhlet method were compared. It appears that

consistent asphaltene samples can be obtained if the following criteria are met:

- (1) Solvent is added at a solvent-to-bitumen ratio greater than 30 cm³/g at room temperature.
- (2) At least 24 h are allowed for equilibration.
- (3) The asphaltenes are Soxhlet washed.

The ASTM D4124 and Soxhlet method meet the above criteria for our work, although the ASTM D4124 method specifies washing the asphaltenes with hot heptane and not necessarily in a Soxhlet apparatus. The IP 143 meets the criteria except for the equilibration time and gave similar asphaltenes although at a lower yield. The Speight method does not meet the criteria and resulted in asphaltenes with different properties. Among the

methods that provide similar asphaltenes, the Soxhlet method has the most clearly defined washing step and gives the highest asphaltene yield and is therefore recommended.

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