

## The Effect of Cosolubilizing Lighter Components on the Asphaltene Content of Heavy Oils

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### Introduction

Asphaltenes are precipitates that separate from petroleum, petroleum residua or bituminous materials on treatment with low-boiling liquid hydrocarbons<sup>1</sup>. The solvents for effecting this separation are n-pentane and n-heptane, although other light hydrocarbon solvents have also been used<sup>2</sup>. The amount and composition of asphaltene fractions are important from processing considerations. In petroleum refining, asphaltene fractions can precipitate in heat exchangers and/or can deposit on catalysts causing excessive coke formation. A number of physical properties of the crude oils are also determined by the asphaltenes. In petroleum production operations, asphaltenes can precipitate and cause extensive formation damage. Asphaltene precipitation in oil reservoirs has proved to be a difficult problem to define and study<sup>3,4</sup>.

Speight<sup>1</sup> provided a detailed discussion on the influence of solvent type on asphaltene separation. Yields of precipitate using various solvents and a western Canadian bitumen indicated that when the solvent carbon number was increased, the yields (wt% bitumen) decreased. This was particularly true for the n-alkane homologous series and was applicable to a lesser degree to naphthenic and aromatic compounds. The amount of precipitate correlated well with two types of solubility parameters defined by the following equations:

$$\delta_i = \gamma V^{-1/3} \quad (1)$$

$$\delta_2 = \left( \frac{\Delta H^v - RT}{V} \right)^{1/2} \quad (2)$$

where,  $\gamma$  is the solvent surface tension,  $V$  is the molar volume,  $\Delta H^v$  is the heat of vaporization,  $R$  is the universal gas constant and  $T$  is the absolute temperature. Burke et al.<sup>3</sup> used Equation 1 to define solubility parameters.

Fractionation of asphaltenes using solvent mixtures also exhibited varying yields depending on the ratio of the solvents used<sup>2</sup>. This data suggests that the amount of asphaltene precipitate will be influenced by the lighter cosolubilizing components in the petroleum or bitumen. The work reported in this paper on the continuous supercritical fluid extraction (SFE) of an oil sands bitumen with propane provides direct evidence on the influence the lighter components have in keeping the asphaltene fractions in solution.

## Experimental

The SFE system was custom-built for the University of Utah by Autoclave Engineers, Inc. A schematic of the apparatus is shown in Figure 1. Central to the system was a temperature controlled extractor with a capacity of 300 cc and rated to a pressure of 37 MPa at 615 K. The extractor was equipped with a magnetic-drive packer-less stirring device. Propane was charged into the extractor and the system was brought to the desired pressure using a high-pressure liquid pump. Pressure control is achieved by incorporating a back pressure regulator in parallel with the pump. The pump-head was cooled by a circulating cooling bath to ensure that the propane was maintained in a liquid state at the pump-head.

Initially 50 g of Whiterocks native bitumen was charged into the extractor. Selected properties of the bitumen are presented in Table 1. Once the initial equilibrium state was attained, propane was continuously pumped into the extractor. Commercial grade propane containing about 96% propane and

4% of other C<sub>1</sub> - C<sub>4</sub> hydrocarbon gases was used in this work. A heated metering valve was used to transfer the extracted phase from the extractor to the separator. The separator was held at ambient pressure. The solvent separated from the extract phase in the separator was vented through a flow totalizer which measured the cumulative volume of solvent withdrawn from the separator. The oil in the separator was collected and weighed. In all the experiments, a known amount of bitumen was charged into the extractor and the continuous extraction process was started. After about 25 liters of solvent (at room temperature) had passed through the totalizer, the amount of oil accumulated in the separator was collected and weighed. When the amounts of oil extracted became small relative to the amount extracted in the first 25 liters, the extraction was stopped. The extractor was depressurized and the residue was weighed and analyzed for maltenes and asphaltenes. In each extraction sequence, seven to eight extract samples were collected, each sample corresponding to an *extraction window* of 25 liters of propane vented through the totalizer or about 20 minutes of extraction time.

Asphaltene contents of the residual fractions produced during the propane extraction of the native bitumen were measured by the analytical method developed by AOSTRA<sup>5</sup>. Two grams of the residual oil sample were dissolved in an equal volume of toluene. Forty volumes of n-pentane were added for each volume of toluene. The AOSTRA method recommends benzene as the diluent; however, toluene was used in place of benzene for safety reasons. The precipitate was filtered from the solution, dried and weighed.

## Results and Discussion

Experiments were performed at three different pressures (5.5 MPa, 10.3 MPa and 17.2 MPa) at a constant temperature of 380 K and at three different temperatures (339 K, 380 K and 422 K) at a constant pressure of 10.3 MPa. The critical temperature of propane is 369.8 K and its critical

pressure is 4.25 MPa. The effect of pressure on the extraction yields at 380 K is presented in Figure 2 and the effect of temperature on the extraction yields at 10.3 MPa is shown in Figure 3. Attempts have been made to link the extraction performance of dense gases to solvent density<sup>6,7</sup>. The densities of pure propane at the experimental conditions, as calculated by the Peng-Robinson equation of state<sup>8</sup> is presented in Table 2. It can be observed from Figures 2 and 3, and Table 2 that density did affect the extraction yields. However, pure solvent density was not the only parameter that governed the extraction process. The density variations for an increase in pressure from 5.5 MPa to 17.2 MPa at a temperature of 380 K and for an increase in temperature from 339 K to 422 K at a pressure of 10.3 MPa were almost identical (44%). However, Figures 2 and 3 indicated that pressure appeared to have a stronger influence on the extraction yields than temperature. The highest extraction yield was obtained at 380 K and 17.2 MPa.

The compositional variation in the extracted material as a function of time can be determined by examining the carbon number distributions of the first, middle and the last extracts for the experiments at 10.3 MPa and 380 K (Figure 4). The middle and the last extracts contained compounds heavier than the first fraction. The carbon number distributions of the middle extracts as a function of pressure (Figure 5) indicated that heavier compounds are extracted at higher pressure. No significant compositional changes in the middle extracts were observed as a function of temperature (Figure 6). This behavior appeared to be consistent with the extraction yield information, where it was observed that pressure had a stronger influence on the extraction process than temperature in the range of pressures and temperatures examined in this work.

Residual oils from all the extraction experiments were dark black solids. The asphaltene contents of the residual oils are listed in Tables 3 and 4 along with the elemental analyses of the residual oils. It should be noted

that the asphaltene content of the feed material was 5.9%. The asphaltene contents of all the residual oils were significantly higher than the original heavy oil. The asphaltene content of the residual oils increased with pressure. This was consistent with the observation that increased extraction of heavier compounds occurred as the extraction pressure was increased. The highest asphaltene content was found in the residual oil from the extraction at 380 K and 17.2 MPa where the extraction yield was also the highest. The asphaltene contents of the extracts were not measured in this study. The percentage of asphaltenes as a fraction of the original oil feed are also listed in Tables 3 and 4. These values were also considerably higher than the asphaltene content of the original oil. Obviously, compounds that did not precipitate from the original oil as pentane insolubles were precipitating from the residual oils.

These experiments established the fact that asphaltenes, as defined in this study (pentane insolubles), are not a definite compound class but were a collection of compounds specific to a given mixture. Lighter compounds in these mixtures helped keep the asphaltene fraction in solution when a pentane solubility test was performed on the mixture. During the extraction process, these lighter compounds were stripped from the original mixture, thus decreasing the tendency of the heavier molecules to be in solution. As a result of this, the pentane insolubles fraction increased in the residual oils. It is apparent from this reasoning that the asphaltene content of the residual oils would be higher for the residuals produced at conditions that led to more efficient extraction of the lighter components. The data demonstrated this with the exception of the extraction at 5.5 MPa and 380 K. In this experiment, despite an extraction of only about 20% of the material which consisted of relatively lighter compounds (Figures 2 and 5), an asphaltene fraction of 14% was observed in the residual oil. Extractions in the vicinity of the critical temperature of propane ( $T_c$  for 380 K is 1.03) and the quality of the compounds extracted may explain this data point. However, detailed

compositional information on the extracts (possibly by gas chromatography - mass spectrometry), their asphaltene contents, etc. would be required to evaluate this.

The elemental analysis of the residual oils reported in Tables 3 and 4 indicated that the H/C ratio of the residual oils decreased relative to the H/C ratio of the original bitumen. This suggested that saturated compounds are preferentially extracted by propane and that the heavier portion of the bitumen is relatively more unsaturated than the bitumen as a whole. It was also seen from the data that the nitrogen and sulfur contents of residual oils were higher than the original bitumen. This indicated that the heteroatomic species are concentrated in the unextractable heavier portion of the bitumen.

The solubility parameters (Equations 1 and 2) increase with carbon number<sup>1</sup>. As the extraction pressure increased more of the heavier hydrocarbons are extracted (Figures 2 and 5). Thus the increase in the asphaltene content of the residual oils for increased extraction pressures was expected. The effect of solubilizing co-solvents<sup>2</sup> led us to presume that as lighter components are extracted, more of the heavier components ought to precipitate. Thus the data reported in this work were intuitive. However, the data did point out that it would be misleading to perform material balances on the asphaltene portions of the fractionated oils (as reported by Burke et al.<sup>3</sup>) since the type and amounts of asphaltenes in different fractions would depend on the solubility character of the specific fractions. Since residual oils recovered in the extractions were dark black solids, it may be wrong to presume that only the pentane insolubles asphaltene fraction of the original oil is susceptible to precipitate in any given recovery or refining process. The solubility parameter approach would also have to be modified to account for the different compound types that precipitate depending on the state of the mixture.

## Conclusions

1. When an oil sand bitumen was subjected to supercritical extraction with propane, the residual oils left in the extractor exhibited significantly higher values of asphaltene fractions than the original oil (bitumen). The loss of cosolubilizing lighter components from the original oil during the extraction process caused more of the heavier components to precipitate thus increasing the apparent asphaltene content. This established that pentane-insoluble asphaltenes were not a definite compound class and that their nature and quantity in a given mixture was determined by the overall solubility character of the mixture.
2. As the extraction pressure increased at a constant temperature of 380 K, the asphaltene content of the residual oil also increased. This was consistent with the observation that the extraction yields increased with pressure and that heavier compounds were extracted at higher pressures.
3. The H/C ratio in the residual oils was lower than the original oil establishing that saturated compounds were preferentially extracted leaving the residual oils richer in unsaturated compounds than the original oil. The nitrogen and sulfur contents of the residual oils were also higher which indicated that heteroatomic compounds concentrated in the heavier (unextractable) portion of the original oil.
4. This study indicated that care should be exercised when performing material balances on asphaltenes from fractionated oils and that it may be inappropriate to presume that only the pentane-insoluble asphaltene fractions of the original oils are susceptible to precipitate in a given recovery (enhanced oil recovery) or refining process.

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**Table 1**  
**Selected Properties of the Whiterocks Bitumen**

Specific Gravity (288 K)	0.98
Conradson Carbon (wt%)	9.50
Pour Point, K	327
Viscosity (323 K), Pa-s	27
<b>Simulated Distillation</b>	
Volatility, Wt%	32.5
IBP, K	520
IBP-477 K, Wt%	0.0
478-616 K, Wt%	5.6
617-811 K, Wt%	26.9
> 811 K, Wt%	67.5

**Table 2**  
**Densities of Propane ( $\text{g cm}^{-3}$ ) at Experimental Conditions**  
**Calculated by the Peng-Robinson Equation of State**

Temperature (K)	339	380	422
<b>Pressure</b>			
5.5 MPa	-	0.2585	
10.3 MPa	0.4782	0.3825	0.2672
17.2 MPa	-	0.4416	-

**Table 3**  
**Selected Properties of the Residual Oils After**  
**Propane Extractions of Bitumen: Pressure = 10.3 MPa**

Extraction	Bitumen		
Temperature (K)	339	380	422
<b>Product Yield(%)</b>			
Extract Phase	40	39	24
Residual Phase	59	58	73
<b>Asphaltene/Maltene</b>			
Asphaltenes, Wt%	12.5	15.0	9.8
Maltenes, Wt%	87.5	85.0	90.2
Asphaltenes Wt% Original Oil	7.4	8.7	7.16
5.9			
<b>Elemental Analysis</b>			
C, Wt%	86.74	86.69	86.66
H, Wt%	10.81	10.80	11.08
N, Wt%	1.95	2.02	1.79
S, Wt%	0.50	0.49	0.47
H/C Atomic Ratio	1.50	1.49	1.53
1.56			

**Table 4**  
**Selected Properties of the Residual Oils After**  
**Propane Extractions of Bitumen: Temperature = 380 K**

Extraction	Bitumen		
Temperature (K)	339	380	422
<b>Product Yield(%)</b>			
Extract Phase	20	39	48
Residual Phase	79	58	50
<b>Asphaltene/Maltene</b>			
Asphaltenes, Wt%	14.0	15.0	20.2
Maltenes, Wt%	86.0	85.0	79.8
Asphaltenes Wt% Original Oil	11.0	8.7	10.1
5.9			
<b>Elemental Analysis</b>			
C, Wt%	86.78	86.69	86.80
H, Wt%	10.97	10.80	10.58
N, Wt%	1.78	2.02	2.12
S, Wt%	0.47	0.49	0.50
H/C Atomic Ratio	1.52	1.49	1.46
1.56			

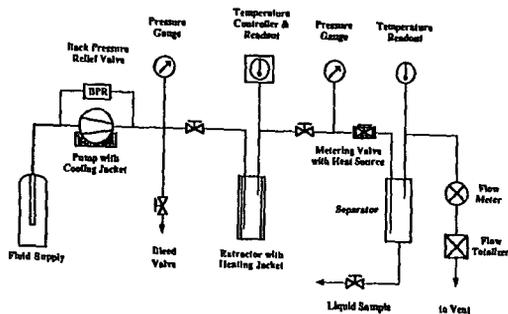


Figure 1: Schematic diagram of the supercritical fluid extraction system

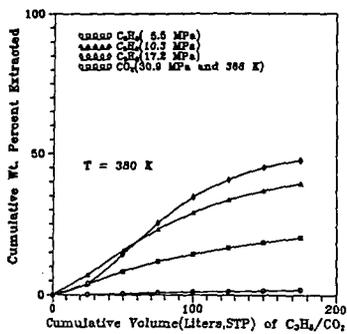


Figure 2: Extraction yields for the native bitumen with propane as function of pressure at 380 K.

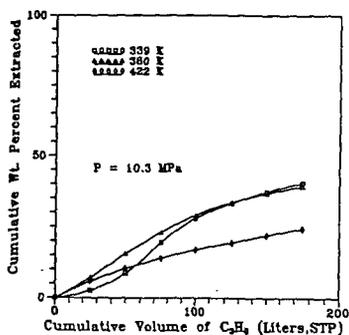


Figure 3: Extraction yields for the native bitumen with propane as function of temperature at 10.3 MPa.

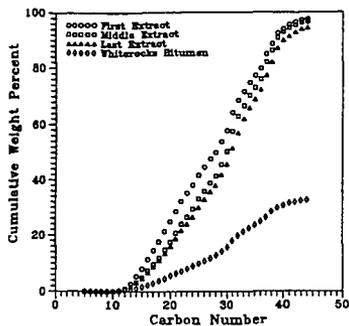


Figure 4: Changing compositions as a function of time for the native bitumen propane extracts at 380 K and 10.3 MPa.

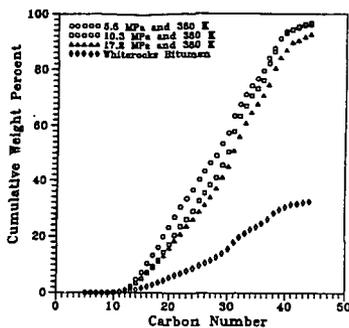


Figure 5: Compositional changes as a function of pressure for the native bitumen propane extractions at 380 K.

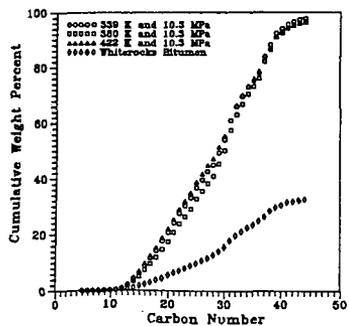


Figure 6: Compositional changes as a function of temperature for the native bitumen - propane extractions at 10.3 MPa.