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Asphaltene Rejection from Bitumens via Supercritical Fluid Extraction

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Abstract

Supercritical fluid extraction (SFE) of bitumen was carried out in a continuous extractor using propane as the solvent at several temperatures and pressures. The asphaltene contents of the residual fractions in the extractor were compared to the asphaltene content of the original bitumen. Asphaltenes were defined as pentane insolubles in this study. It was found that the absolute asphaltene content of the residual fractions exceeded the asphaltene content of the original bitumen. Even when the asphaltene content was prorated by the weight percent of the residual material, it was found to be higher than the original asphaltene content. The data established that the types of compounds separating as asphaltenes changed as the nature of the mixture was altered by SFE. The data also indicated that it may be inappropriate to perform asphaltene material balances to assess the amount of precipitate. The original asphaltene content of a bitumen that is undergoing compositional changes in a sequence of operations may not be an accurate measure of the precipitating tendency of the bitumen in production and processing operations.

The asphaltene content of the residual material varied depending on the extraction conditions and was as much as 3-5 times the original asphaltene content. The asphaltene content of the residual material was a maximum at the most efficient extraction condition which was in the vicinity of the critical temperature of propane. The H/C atomic ratio of the residual fractions was lower compared to the original bitumen, indicating that the ratio of polar to nonpolar compounds may also be important from precipitation considerations. Saturate and aromatic compounds were preferentially extracted and the ratio of asphaltenes to resins increased in the residual fractions relative to the original bitumen.

Introduction

Asphaltenes are precipitates that separate from petroleum, petroleum residua or bituminous materials upon treatment with low-boiling hydrocarbon solvents¹. Asphaltenes in petroleum mixtures are of concern in petroleum processing since they are believed to contribute to coke formation and catalyst deactivation, and to equipment damage. It is believed that the asphaltene content of heavy oils and bitumens is a key index related to processibility. It is therefore desirable to separate or reject the asphaltene fraction prior to processing in situations where asphaltene separation during processing or upgrading operations is viewed as a possibility. This is particularly true in the processing of heavy oils and bitumens. The ROSE^{2,3} process has been employed to reject asphaltenes for the upgrading of resids, heavy oils and bitumens. When such a rejection is effected, it is important to identify the relationship between the rejected material and the parent material. The objective of this work was to characterize the rejected material and compare its chemical composition with the parent material.

The solvents used to separate asphaltenes in standard tests are n-pentane and n-heptane, although other light hydrocarbon solvents have also been used⁴. Speight¹ provided a detailed discussion on the influence of solvent type on asphaltene precipitation for a Canadian bitumen. Yields of precipitate using various solvents indicated that when the solvent carbon number increased, the yields (wt% bitumen) decreased. This was particularly true for the n-alkane homologous series and was also applicable to a lesser degree for naphthenic and aromatic compounds. Yields of asphaltenes using solvent mixtures also varied depending on the ratio of the solvents used⁴. These data suggest that the amount of asphaltene precipitate will be influenced by the lighter cosolubilizing components in the oil or bitumen.

Asphaltenes are defined as compounds that are insoluble in a pentane solubility test. Thus, if the composition of the original oil is altered,

it is likely that the asphaltene content of the altered mixture will change. If this is the case, it may be inappropriate to consider asphaltene material balances for different fractions of the original oil. Furthermore, separation of compounds classified as asphaltene by itself may not be adequate in considering the problem of asphaltene rejection. A broader view of the material that is rejected maybe necessary to define the problem completely. The motivation for this work was to provide insight into some of the above considerations. This paper provides data on the chemical composition of the residual fractions after supercritical extraction (SFE) of a bitumen with propane. The rejection of asphaltenes in this work differs from that in the ROSE process in that the actual extraction is performed at conditions at which the solvent is in its supercritical state, whereas, in the ROSE process, only the solvent recovery is accomplished at supercritical conditions.^{2,3,5}

Experimental

The SFE system was custom-built for the University of Utah by Autoclave Engineers, Inc. Description of the system and the experimental procedures have been discussed by Deo et al.⁶ and by Hwang⁷. Selected properties of the bitumen are presented in Table 1. The asphaltene content of this feed material as determined by the pentane-insolubles test was 2.9 wt%. The saturate and aromatic fraction was 42.7% and the resin content was 54.5%. The SFE was performed using commercial grade propane, containing about 96% propane and 4% C₁, C₂ and C₄ hydrocarbon gases. Extraction was performed at several temperatures and pressures. In each extraction sequence, seven to eight extract samples were collected. Each sample corresponded to an extraction window of 25 liters of propane vented through the the separation system or about 20 minutes of extraction time. The samples were weighed and their carbon number distributions were determined by simulated distillation. Each of the sample was analyzed for

its asphaltene, resin and saturate and aromatic content. The H/C ratio was also obtained for each of the samples.

Table 1
Selected Properties of the
Whiterocks Heavy Oil

Specific Gravity (288 K)	0.98
Conradson Carbon Residue (wt%)	9.5
Pour Point, K	327
Viscosity (323 K), Pa-s	27
Asphaltenes, wt% (Pentane Insolubles)	2.9
Saturates and Aromatics	42.7
Resins	54.5
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

Asphaltene contents of the residual fractions produced during the propane extraction of the bitumen were measured by the analytical method developed by AOSTRA⁸. Two grams of the residual fraction 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 environmental reasons. The precipitate was filtered from the solution, dried and weighed. Saturate and resin fractions of all the samples were determined by a procedure described by Bukka, et al.⁹

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.⁷ The critical temperature of propane is 369.8 K and its critical pressure is 4.25 MPa. It was observed that the extraction yields increased as a function of pressure at constant temperature. However no clear trend was observed as a function of temperature at constant pressure. Attempts have been made to link the extraction performance of dense gases to density.^{10,11} Increased extraction yields with respect to pressure are consistent with the recognition that pure solvent density in the vicinity of its critical temperature strongly affects extraction⁵. Trend with respect to temperature demonstrates that pure solvent density is not the only governing parameter. Direct evidence for this observation is presented in Figure 1, where the extractions at two different pure solvent reduced densities are compared. Enhanced extraction behavior is observed at a lower solvent reduced density. This behavior is possibly related to the phase behavior of the propane-bitumen system just above the critical temperature of propane. It should be noted that the highest extraction yield was obtained at 380 K and 17.2 MPa.

Examination of the compositional variation in the extracted material as a function of time showed that the middle and the last extracts contained compounds heavier than the first fraction. Compositional variation in the extract phases as a function of pressure indicated that heavier compounds are extracted at higher pressure (Figure 2). Thus, as the extraction efficiency increased (at higher pressures and thus higher reduced densities), heavier compounds were found in the extracts. Compositional changes in the middle extracts as a function of temperature showed that the heaviest compounds were extracted at 380 K, where the extraction efficiency was also the highest. Thus, the composition information on

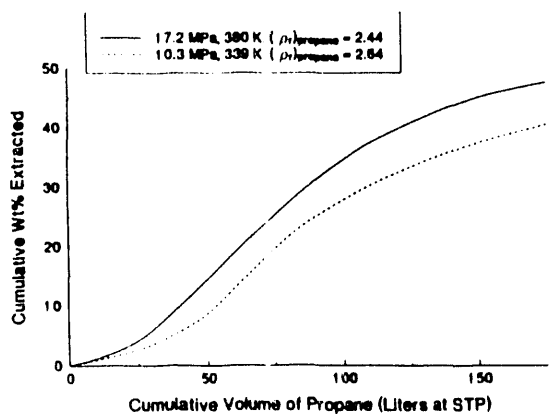


Figure 1: Extraction of Whiterocks bitumen by propane at two different propane densities: Enhanced extraction at lower propane reduced density.

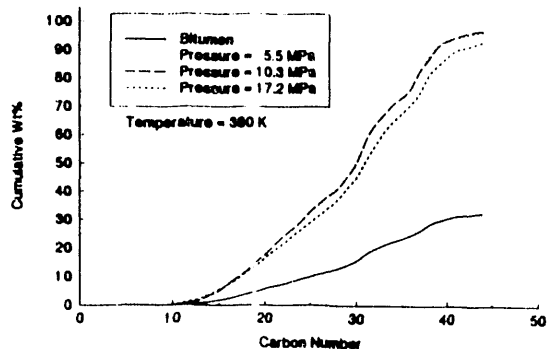


Figure 2: Composition of the middle extracts obtained at different pressures indicating that heavier compounds are extracted at higher pressures.

the extracted fractions was consistent with the extraction yield data.

Residual fractions from all the extraction experiments were dark black solids. Comparisons of the chemical-type and elemental analyses of the residual fractions with those of the original bitumen are presented in Figures 3-10. In the resin-asphaltene analyses, material balances ranging from 98% to 101% were realized. The yields of asphaltenes, saturates and aromatics and resins were normalized to 100%.

It should be noted that the asphaltene content of the feed material was 2.9%. The asphaltene contents of all the residual fractions were significantly higher than the original bitumen (Figures 3 and 4). The asphaltene content of the residual fractions 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 fraction 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 bitumen feed are also presented in Figures 3 and 4. These values were also considerably higher than the asphaltene content of the original bitumen. Obviously, compounds that did not precipitate from the original bitumen as pentane insolubles were precipitating from the residual fractions.

Comparison of the saturates and aromatics in the residual fractions with the saturates and aromatics in the original bitumen (Figure 5) revealed that the saturates and aromatics were preferentially depleted from the original bitumen. It was observed (Figure 5) that at higher pressures, as the extraction efficiency increased, more of the saturates and aromatics were extracted from the original bitumen. In fact, for the extraction at 380 K and 17.2 MPa, the amount of saturates and aromatics in the residual fraction was found to be zero. The amount of saturates and aromatics were seen to increase in the residual fractions (Figure 6) as a function of temperature at constant

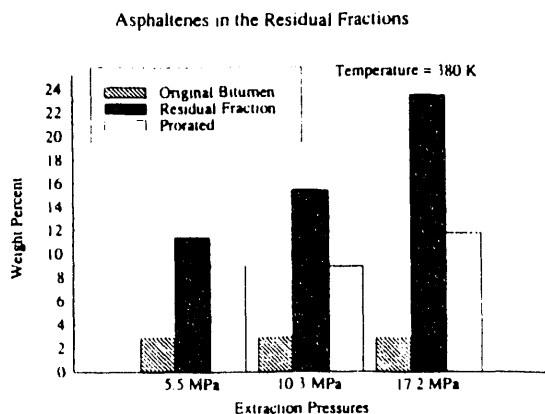


Figure 3: Comparison of the asphaltene contents of the residual fractions with the asphaltene content of the original bitumen: Varying pressure at constant temperature.

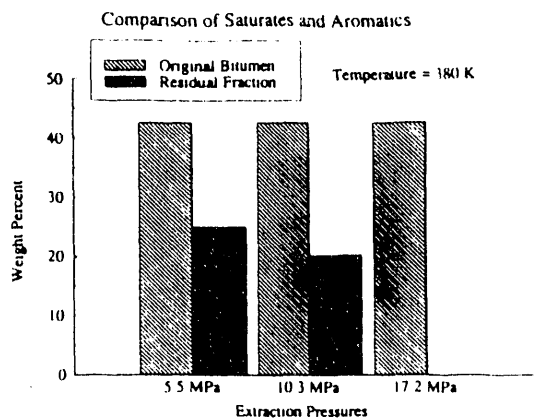


Figure 5: Comparison of the saturates and aromatics in the residual fractions with the saturates and aromatics in the original bitumen: Varying pressure at constant temperature.

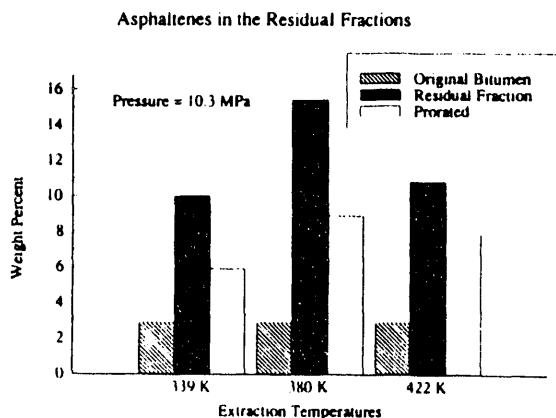


Figure 4: Comparison of the asphaltene contents of the residual fractions with the asphaltene content of the original bitumen: Varying temperature at constant pressure.

pressure.

A comparison of the resins in the residual fractions with the resins in the original bitumen revealed that the resin content of the residual fractions increased with extraction pressure (Figure 7). This observation was consistent with the fact that saturates and aromatics were preferentially extracted from the residual fractions leaving them relatively richer in resins. This observation was further confirmed by examining the resins in the residual fractions as a function of temperature at constant pressure (Figure 8).

The H/C ratios of the residual fractions have been compared to the H/C ratio of the bitumen in Figure 9. The H/C ratios of the residual fractions are consistently lower than the H/C ratio of the original bitumen, suggesting that the residual fractions are more polar than the bitumen. It was also observed from Figure 9 that as the extraction pressure increased (as the extraction became more severe) the H/C ratio of the residual fractions decreased. This observation was consistent with

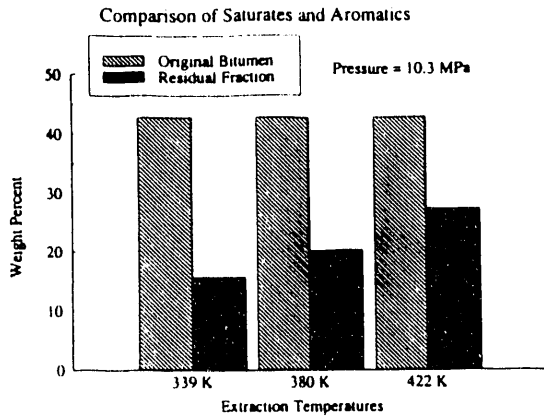


Figure 6: Comparison of the saturates and aromatics in the residual fractions with the saturates and aromatics in the original bitumen: Varying temperature at constant pressure.

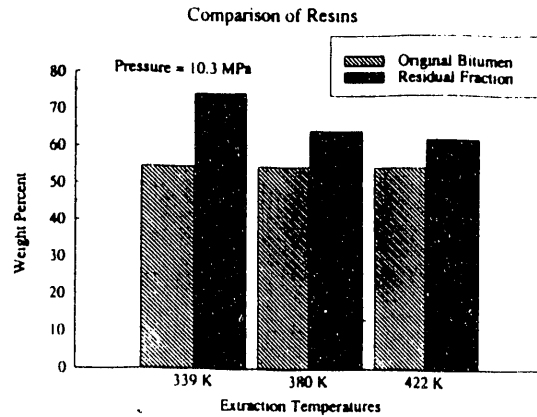


Figure 8: Comparison of the resins in the residual fractions with the resins in the original bitumen: Varying temperature at constant pressure.

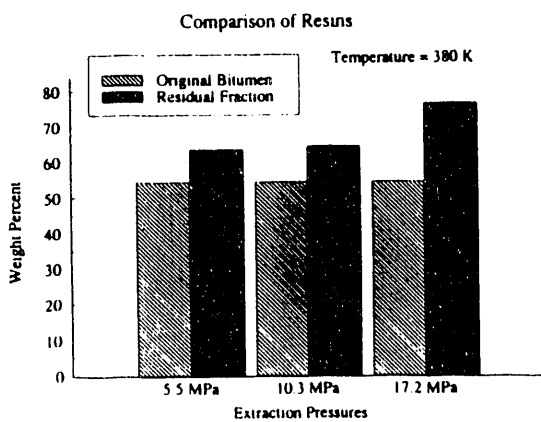


Figure 7: Comparison of the resins in the residual fractions with the resins in the original bitumen: Varying pressure at constant temperature.

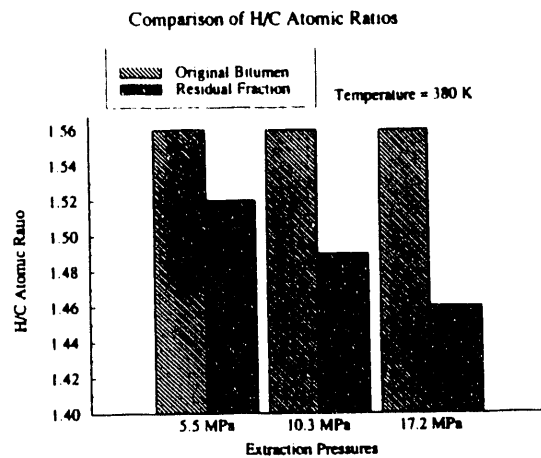


Figure 9: Comparison of the H/C ratios of the residual fractions with the H/C ratio of the original bitumen: Varying pressure at constant temperature.

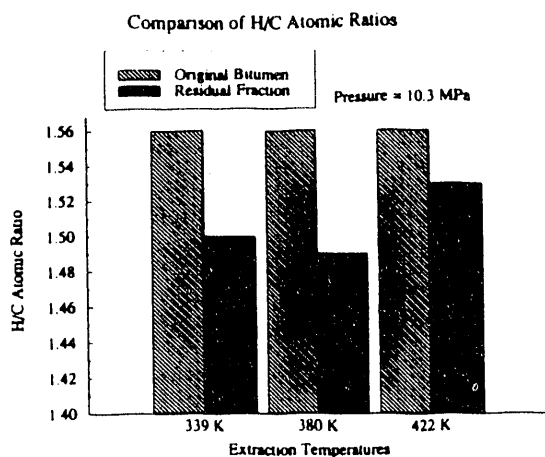


Figure 10: Comparison of the H/C ratios of the residual fractions with the H/C ratio of the original bitumen: Varying temperature at constant pressure.

the observation that the saturates and aromatics contents of the residual fractions decreased with increased extraction pressures (Figure 5). Examination of the H/C ratios of the residual fractions with respect to increasing extraction temperatures (Figure 10) revealed that the H/C ratio of the residual fraction obtained at 380 K was the lowest. The extraction had been observed to be the most efficient at 380 K, a temperature that was closest to the critical temperature of the solvent.

Selected high-temperature simulated distillation analyses were performed on some residual fractions. A short 15 m capillary column was used for these experiments. The end point for these analyses was 993 K (1328°F) corresponding roughly to a carbon number of 100. A comparison of the boiling point distributions of two of the residual fractions with the high-temperature boiling point distribution of the original bitumen is presented in Figure 11. The figure graphically demonstrates the depletion of compounds over a wide carbon number range from the original bitumen. It is this depletion that leads to the significant increase in

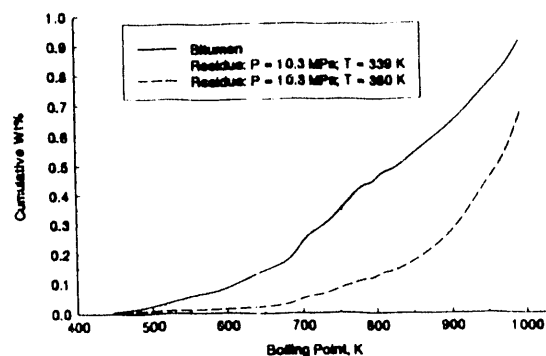


Figure 11: Comparison of the carbon number distributions (obtained using high-temperature simulated distillation) of a few residual fractions with that of the original bitumen.

the asphaltene content of the residual fractions. It is also observed that the residual fraction at 10.3 MPa and 380 K is heavier than the residual fraction at 10.3 MPa and 339 K. This is consistent with the observations that heavier compounds were extracted at 380 K and that the asphaltene content of the residual fraction at 380 K was higher.

These experiments established the fact that asphaltenes, as defined in this study (pentane-insolubles), are not a definite compound class but are 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 remain in solution. As a result of this, the pentane-insolubles fraction increased in the residual fractions. It is apparent from this reasoning that the asphaltene content of the residual fractions would be higher for the residu-

als produced at conditions which would lead to more efficient extraction of the lighter components.

The effect of solubilizing co-solvents⁴ led us to presume that as lighter components are extracted, more of the heavier components ought to separate. Kawanaka et al.¹² hypothesize that essentially two factors are responsible for maintaining the mutual solubility of compounds in petroleum crudes:

1. Ratio of polar to nonpolar species.
2. Ratio of high to low molecular weight species.

It is seen from the data presented in this paper that SFE alters both the above ratios in the extracted fractions and the residual fractions relative to the original mixture. The data reported in this paper are thus a direct confirmation of the hypothesis of Kawanaka et al.¹² It is obvious that lighter components are being extracted in SFE. The H/C ratio comparisons suggest that the residual fractions are more polar than the original bitumen. Thus the polar-to-nonpolar compound ratio is higher in the residual fractions than in the original bitumen. There is some evidence to suggest that extraction of lighter components alone will not cause an increase in the asphaltene content of the residual fractions. Bukka¹³ found no significant change in the asphaltene content of several bitumens when he distilled and separated the lighter 10 and 20 wt% of the original material. This suggests that alteration of the polar-to-nonpolar compound ratio in the residual fractions may be more important than the depletion of lighter components. On the other hand, depletion of the saturate and the aromatic compounds from the original bitumen is one of the important factors that leads to more of the residual fractions to be classified as *asphaltenes*. The ratio of the asphaltenic-to-resinous compounds increased in the residual fractions relative to the original bitumen. This suggests that it may be necessary to consider colloidal flocculation concepts related to critical resin concentrations (Leontaritis¹⁴) along

with solubility theories in order to understand and predict the rejection of asphaltenes from bitumens and heavy oils.

The data presented in this paper do point out that it may be inappropriate to perform material balances on the asphaltene portions of the fractionated oils and bitumens since the type and amounts of asphaltenes in different fractions would depend on the solubility character of the specific fractions. It may be wrong to presume that only the pentane-insolubles asphaltene fraction of the original bitumen would be rejected in an asphaltene rejection process. The residual fractions were comprised of asphaltenes, resins and other hydrocarbons. It would be essential to consider the rejection of all of the higher boiling compounds in the original bitumen in order to develop a comprehensive understanding of rejection process.

Conclusions

1. When a bitumen was subjected to supercritical extraction with propane, the residual fractions left in the extractor exhibited significantly higher asphaltene contents than the original bitumen. The loss of cosolubilizing lighter components from the original bitumen 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 were 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 fraction 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. Saturate and aromatic hydrocarbons were extracted preferentially relative to resins

and asphaltenes. The asphaltene to resin ratio in the residual fractions was higher compared to that of the original bitumen.

4. The H/C ratio in the residual fractions was lower than the original bitumen establishing that saturated compounds were preferentially extracted leaving the residual fractions richer in unsaturated compounds (and thus more polar) than the original bitumen.
5. This study indicated that care should be exercised when performing material balances on asphaltenes from fractionated oils and/or bitumens and that it may be inappropriate to presume that only the pentane-insoluble asphaltene fractions of the original heavy petroleum materials would be rejected in an asphaltene rejection process.

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