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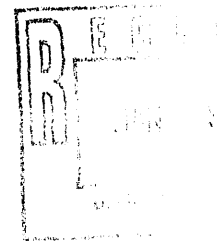
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Characterization of Uinta Basin Oil Sand Bitumens

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Abstract

Results of the analyses of the saturate and monoaromatic fractions of four Uinta Basin bitumens (southwest Whiterocks, northwest Whiterocks, Asphalt Ridge and Sunnyside) are presented in this paper. After separating the bitumen samples into several fractions using solvent extraction and elution chromatography, peak-by-peak analysis was performed on the saturate and monoaromatic fractions using GC-MS. The saturated compounds were predominantly polycyclic naphthenes, while the monoaromatics were mostly naphthenoaromatics. Samples from all of the deposits contained a significant number of compounds in the carbon-number range C_{27} - C_{30} due to the presence of steranes and hopanes. Carbon number and Z-number distributions were produced using sorting and quantitation procedures developed in this project. Although the four samples were believed to be of common origin and maturity, significant differences in carbon-number distributions and chemical-type distributions were shown to exist. Even two samples from the same deposit (Whiterocks) exhibited significant differences. Relative abundances of steranes and of hopanes with a carbon number greater than C_{30} were used as measures of the relative degree of biodegradation of the samples. It was found that biodegradation increased as follows: southwest Whiterocks < northwest Whiterocks < Asphalt Ridge < Sunnyside.

Introduction

Differences in composition between crude oils are generally attributed to one or more of the following: biodegradation, maturity, source, and migration. Biodegradation, in combination with water washing, is a process whereby lighter compounds, including alkanes, isoprenoids and alkylcyclohexanes, are bacterially degraded and removed from the reservoir oil. It is thought to be the major process whereby conventional oils are transformed into oil sand bitumen, and, therefore, a major contributor to compositional variation among deposits¹. Evidence for the severe biodegradation of a Uintah Basin bitumen was presented by Reed².

Thermal maturity can cause significant compositional variations between oils. And, while all of the Uinta Basin oil sand deposits are relatively immature, differences in maturity may be the cause of some of the compositional differences within the basin^{3,4}.

Differences in source and the effects of migration are also known to effect composition. In the Uinta Basin, however, these effects are considered to be relatively minor, since these oils are believed to be of common origin and to have migrated relatively short distances from their source rock.

Experimental Approach

The oil sand samples chosen for this study were from the Whiterocks, Asphalt Ridge and Sunnyside deposits in the Uinta Basin, Utah. Samples from two locations in the Whiterocks deposit were collected⁵. These two samples will be referred to as northwest Whiterocks and southwest Whiterocks.

The bitumens were fractionated into their respective saturate and monoaromatic, polyaromatic, resin, and asphaltene fractions using the separation scheme shown in Figure 1⁶. The fraction containing the saturate and monoaromatic compounds was analyzed by gas chromatography-mass spectrometry (GC-MS). A J & W Scientific DB-1 capillary column was used for all of the analyses. The 30 m long col-

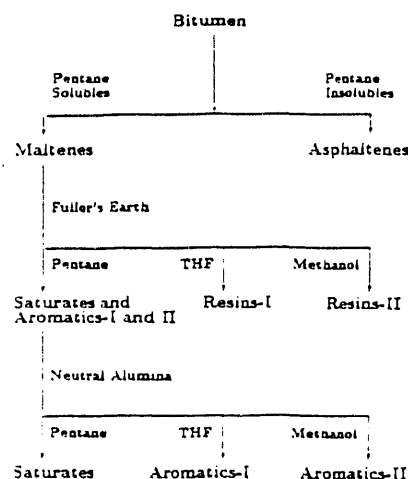


Figure 1: Bitumen Fractionation Scheme

umn was 0.25 mm in internal diameter and was coated with a 0.25 micron film of a polysiloxane bonded phase. The samples were coated onto a Curie-point wire and vaporized into the column. The initial temperature of the column was 30°C. It was heated to a final temperature of 350°C at the rate of 3°C per minute. The mass spectrometer was used in an electron-impact mode and an ion-trap detector was used to obtain spectra of the eluting compounds.

Structural Analysis

Compound identification was accomplished by analyzing the total-ion chromatogram peak by peak using Finnegan's Ion Trap Detector System (ITDS) software⁷. Individual-compound spectra and mass-spectral libraries were used to identify the peaks in the samples. Each sample consisted of about 80-100 compounds. It was assumed that the response factors for each compound were equal and that area percentage was equivalent to weight percentage. The weight-percent information was stored in a data file along with the scan number and identity of each compound type. The molecular weight, the number of carbon atoms per molecule, the number of aromatic and nonaromatic rings per molecule, and the Z number were also recorded. The Z number is

defined as the value of Z in the general hydrocarbon formula C_nH_{2n+Z} .

While the ITDS software was very useful in analyzing individual compound types, it was inadequate for categorizing and sorting compounds according to carbon number, molecular weight, or Z number. A computer program was written in FORTRAN to process such information. The program determines relative abundance according to carbon number, molecular weight, or compound type (i.e., Z number). It can also be used to determine relative abundance vs. carbon number for a particular Z number. In the fractionation process described above, saturated hydrocarbons eluted simultaneously with alkylbenzenes and monoaromatic naphthoenaromatics (jointly classified as monoaromatics for convenience). Using this computer code, saturated hydrocarbons were separated from monoaromatics by normalizing separately for the total peak area in each category.

Carbon-Number Distributions

A plot of cumulative relative abundance vs. carbon number is shown in Figure 2 for samples of saturated hydrocarbons from the three deposits. Over 60% of saturates from Asphalt Ridge are between C_{11} and C_{15} . And over 30% fall between C_{27} and C_{30} . The southwest Whiterocks sample, however, exhibits a much different distribution with only about 15% of its saturates below C_{26} and about 45% between C_{28} and C_{30} . The northwest Whiterocks and Sunnyside samples show strikingly similar curves, with carbon-number distributions mostly between those of the Asphalt Ridge and southwest Whiterocks saturate samples.

A plot of cumulative relative abundance vs. carbon number is shown in Figure 3 for the monoaromatic fraction of each of the four samples. The carbon-number distributions for the monoaromatic fractions show similar trends to those of the saturate fraction. The Asphalt Ridge sample has the lowest average carbon number, while the southwest Whiterocks sample has the highest average carbon

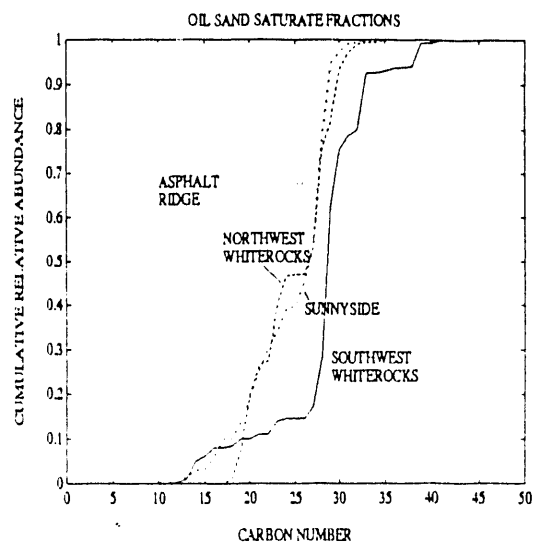


Figure 2: Carbon Number Distribution for Saturate Fractions

number. And, as with the saturate fractions, the carbon-number distributions for the northwest Whiterocks and Sunnyside monoaromatics lie roughly between those of the other two monoaromatic fractions.

Z-Number Distributions

In addition to analysis by carbon-number distributions, Partition can be used to plot relative abundance vs. Z number, where the Z number is defined according to the general hydrocarbon formula, C_nH_{2n+Z} . For the saturate fractions, the Z number can have the values of 0, -2, -4, -6, or -8, representing compounds having 1, 2, 3, 4, and 5 rings, respectively. For the monoaromatic fractions, the Z number can have the values of -6, -8, -10, -12, or -14, representing naphthoenaromatics having 1, 2, 3, 4, and 5 rings, respectively. Thus, the Z number is a measure of the hydrogen deficiency. As the number of rings increases, the Z number becomes more negative, and the hydrogen-to-carbon ratio decreases. It is important to note that only gross structural information such as number of rings, carbon

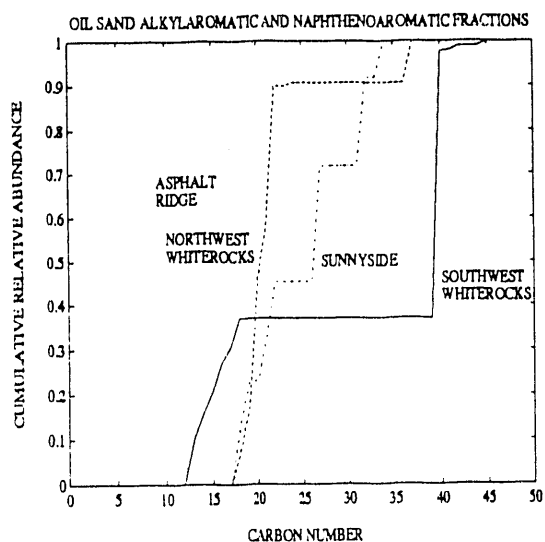


Figure 3: Carbon Number Distribution for Monoaromatic Fractions

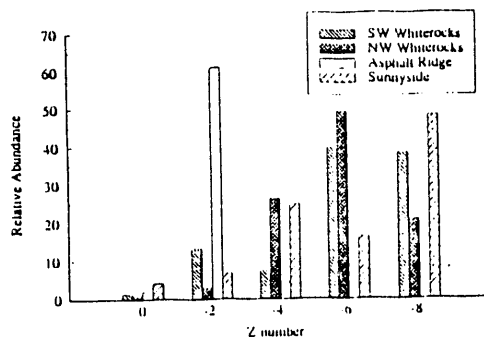


Figure 4: Z Number Distribution for Saturates

number, molecular weight, and Z number was determined in this analysis. Structural detail such as the position of side chains, the length of particular side chains, and stereochemistry was not determined.

The relative abundance vs. Z number for the saturate fractions of each sample is plotted in Figure 4. It is evident that the alkylcyclohexanes are in very low concentration for all of the samples. And while the bicyclics are in relatively low concentration for the White Rocks and Sunnyside samples, they represent over 60% of the Asphalt Ridge sample.

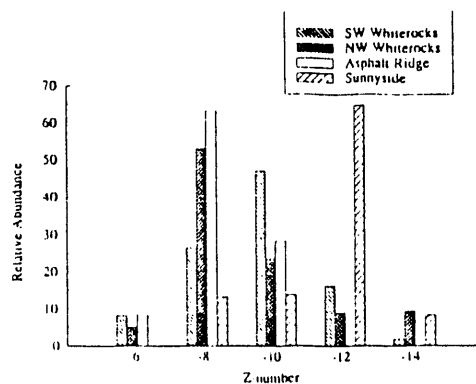


Figure 5: Z Number Distribution for Monoaromatics

The Z-number distribution for the monoaromatic fractions of each sample is shown in Figure 5. It is evident that both the alkylbenzenes and the monoaromatized pentacyclics are in relatively low concentration. As with the saturate fractions, the 2-ring ($Z = -8$) compounds have the highest relative abundance for the Asphalt Ridge sample. The Sunnyside sample shows the domination of 4-ring ($Z = -12$) compounds.

Biodegradation

The compound types found in the saturate and monoaromatic fractions are in a class of chemicals called "biomarkers". As such, they are used to make determinations about the maturity, source, migration, and degree of biodegradation of oil. In general, oil sand bitumens are moderately-to-heavily biodegraded oils, meaning that they are partly-to-completely devoid of n-alkanes, isoprenoids, and alkylcyclohexanes^{8,9,10}. The analyses indicated that, among the saturate samples, n-alkanes and isoprenoids were undetected, while alkylcyclohexanes were present in only trace concentrations. This implies, of course, that the bitumens are devoid of these compound types, since, if they were present, they would have eluted with the saturates.

Since n-alkanes, isoprenoids, and alkylcyclohexanes are absent in heavily biodegraded oils, it is necessary to examine the relative concentrations of compounds that are increas-

ingly more resistant to biodegradation in order to determine the relative degree of biodegradation of bitumens. After the disappearance of n-alkanes, isoprenoids, and alkylcyclohexanes, the next most likely compounds to be biodegraded are steranes^{9,10}. Therefore, as biodegradation increases, the relative abundance of steranes decreases. A similar measure of biodegradation in heavily biodegraded oils is the ratio of C₃₀₊ hopanes to all of the hopanes within a sample^{11,12}. The hopanes with long side chains (i.e., high carbon numbers) are biodegraded preferentially and the hopane C₃₀₊ fraction decreases as the degree of biodegradation increases. Table 1 lists the relative abundance of steranes and the C₃₀₊ fraction for each of the four samples, showing that, by both of these measures, the degree of biodegradation progresses steadily from southwest Whiterocks to Sunnyside.

Table 1
Relative Degree of Biodegradation of Uinta Basin Bitumens

Deposit	Sterane Fraction	Hopane C ₃₀₊ Fraction
Southwest Whiterocks	0.139	0.379
Northwest Whiterocks	0.112	0.259
Asphalt Ridge	0.054	0.133
Sunnyside	0.029	0.013

Conclusions

Carbon-number and Z-number distributions were determined for the saturate and monoaromatic fractions from 4 samples representing 3 oil sand deposits in the Uinta Basin, Utah. A wide inter-deposit variation in compound type was observed for both the saturates

and monoaromatics. Likewise, a significant variation in compound-type distribution and carbon-number distribution was evidenced for 2 samples from the Whiterocks deposit. These differences in distribution might be due, in part, to the relative degree of biodegradation of each sample. Two biodegradation parameters, the sterane fraction and the hopane C₃₀₊ fraction, suggest an increase in the relative degree of biodegradation as follows: southwest Whiterocks < northwest Whiterocks < Asphalt Ridge < Sunnyside.

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