

The Chemistry of the Alberta Oil Sand Bitumen

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Bitumen chemistry is a complex field and poses a considerable challenge to the chemist. Bitumens are known to be comprised of an exceedingly large number of organic molecules which, in the case of the Alberta oil sand bitumen (AOSB), range from the simplest organic molecule, methane, to large polymeric molecules having molecular weights in excess of 15,000. In the AOSB hundreds of organic molecules representing paraffinic, olefinic, aromatic and heterocyclic structures with various functional groups have been identified. Most of these molecules are neutral but some have acidic or basic functions and are capable of salt formation. Others, by virtue of their skeletal or functional reactivity, may form π -bonded, hydrogen bonded or charge transfer complexes. While most of the constituent molecules are stable, some are relatively unstable and can undergo thermal decomposition even well below room temperature. Indeed, it has been demonstrated in recent studies that slow thermal processes are taking place in some of the major Alberta oil sand formations. These reactions are accelerated by the catalytic effect of the mineral matter present in the bitumen.

What distinguishes bitumen from conventional petroleum is the small concentration of low molecular weight hydrocarbons present and the abundance of high molecular weight polymeric materials. The latter are amorphous solids which are dissolved in colloidal form in the lower molecular weight liquid constituents, endowing the bitumen with a viscous, syrupy consistency. The high molecular weight solids are soluble in liquid aromatics such as benzene or toluene and insoluble in low molecular weight paraffins and therefore can be separated from the bitumen by *n*-pentane precipitation from a benzene solution of the bitumen. The solid precipitated this way is called asphaltene. It is evident that such an operational definition of the asphaltene based entirely on solubility may group together a large number of structurally unrelated molecules. Current studies provide clear evidence that the polymeric framework of the asphaltene molecules derived from various sources may be quite different.

Most asphaltenes are rich in heteroatoms, oxygen, nitrogen and especially sulfur. The asphaltene content of the AOSB is in the 16-25% range and the asphaltene contains ~80%C; 8.0%H; 8-9%S, 2.5%O; and 1.0%N.

The main difficulty associated with underground recovery of the AOSB is the consequence of the extremely high viscosity of the bitumen for which the asphaltene is mainly responsible. Therefore, in order to develop a rational approach to the conceptual understanding and practical resolution of the problem one must start with the study of asphaltene itself. The molecular structure of this material has not yet been fully understood and is still the subject of some conjecture. Apart from its pertinence to *in situ* recovery technology, knowledge of the molecular structure of asphaltene is the key to its possible future commercial utilization, to the elucidation of its origin and diagenetic history, and may conceivably shed some light on the history of the bitumen formations.

The chemical composition of the deasphalted bitumen, the maltene, is also of interest from both a practical and conceptual point of view. This fraction represents the bulk of the bitumen and is one of the major factors which determine the commercial value of the separated bitumen. Detailed

knowledge of the chemical composition of this fraction in conjunction with geological and microbiological data will ultimately lead to the unravelling of the mystery of the source and origin of the bitumen formations of Alberta, the relation between the various major oil sand deposits and their interrelation with conventional oil accumulations of the region.

The Thermal Maturation Process.

The realization that a slow, thermal maturation is presently occurring in the bitumen formations of Northern Alberta was the ultimate conclusion of a recent kinetic study of the low temperature thermal behaviour of the oil sand [1-4].

The oil sand in its natural state was shown to contain small quantities of volatile hydrocarbons, methane, propane, propylene and, curiously, neopentane, together with some acetaldehyde. The latter molecule is too reactive to survive long periods of time in the oil sand and must have been formed relatively recently. Heating of the oil sand under controlled conditions resulted in the production of additional amounts of the volatiles present originally in the sand and also some new products. The amounts of gases in question are small, in the ppb-ppm range, nonetheless they can be measured with reasonable accuracy. Thus, measurements of gas evolution at moderately high temperatures provided a key to the detection and monitoring of chemical changes which take place in the oil sand. In the course of the measurements it was found that the rate of evolution of gases, hydrocarbons, acetaldehyde, CO₂, CO, H₂S, COS, CS₂, SO₂, etc., obeyed Arrhenius' law which made it possible to determine the activation energy and preexponential factor for the production of each gas. The activation energies were all low, 5-23 kcal/mole, and the preexponential factors high. From these Arrhenius parameters it was then possible to determine the rate constant for the evolution of each gas in the formation at the formation temperature, 5°C. This in turn made it possible to estimate the time interval required for the accumulation of the quantity of gases present. The results indicate time periods from several days to several months and therefore we are forced to conclude that a slow thermal maturation is taking place presently in the Athabasca oil sand formation and the measured concentration of gases represent a steady state distribution governed by the rate of formation and rate of loss by chemical reactions and/or diffusion. The role of microbial degradation as compared to the thermal processes appears to be negligible.

The total amount of gases released is small and even at 210°C comprises only a few tenths of one percent of the bitumen. But because the volatilized fragment represents a relatively small proportion of the molecules affected by the decomposition, the fractional amount of bitumen still capable of undergoing maturation would be much higher, probably in the order of several percent.

Similar studies on the separated bitumen, asphaltene and maltene, have indicated that the mineral matter present in the oil sands acts as a catalyst for decomposition and that maltene and asphaltene behave in a similar manner but the activation energies associated with their decomposition are significantly higher than those of the whole oil sand. For a better understanding of this maturation process it will be necessary to extend these studies to all major oil sand deposits, examine the relation between reactivity and depth, identify reactive precursors such as those of neopentane and acetaldehyde and to improve the reproducibility and accuracy of the experimental techniques employed.

At present virtually no information exists on the magnitude or composition of the gas accumulations in the oil sand although this would be extremely important in order to understand what is transpiring in the formations.

The results of current similar studies on the Cold Lake formation indicate an analogous thermal behaviour for the bitumen. The total amounts of volatile hydrocarbons produced in the formations are difficult to estimate, but may be in the range of 10^5 - 10^6 tons annually. A fraction of this would undoubtedly escape into the atmosphere and influence the air quality of the region.

The Chemical Composition of the Maltene.

The composition of maltene, the deasphalted bitumen, has been investigated by the API-60 procedure, a somewhat simplified version thereof and also by microanalytical procedures developed in organic geochemical studies [5-7].

The elemental compositions of Peace River, Wabasca, Athabasca and Cold Lake bitumens are given in Table I, and Table II gives their gross composition according to classes.

TABLE I
Overall Composition of Alberta Oil Sand Bitumens [5-7]

Fraction	Source*	%					H/C	mw
		C	H	N	O	S		
Whole Bitumen	A	83.98	10.22	0.65	1.97	4.57	1.46	620
	P	81.68	9.98	0.14	2.08	5.60	1.46	520
	C	83.93	10.46	0.23	0.94	4.70	1.49	490
	W	82.44	10.32	0.42	0.82	5.51	1.49	600
Asphaltenes	A	81.31	7.88	1.06	2.79	7.53	1.16	5,920
	P	79.87	8.15	0.78	2.08	8.82	1.21	3,500
	C	80.54	7.39	1.15	1.78	6.51	1.10	8,140
	W	80.46	8.20	0.99	1.16	8.40	1.21	5,760
Deasphalted Oil	A	84.38	10.63	0.07	0.87	3.91	1.51	435
	P	82.89	10.61	0.08	1.27	5.41	1.53	440
	C	84.19	11.01	0.27	0.61	3.89	1.54	430
	W	82.99	10.74	0.28	1.04	5.25	1.54	530

* A=Athabasca, P=Peace River, C=Cold Lake, W=Wabasco bitumen.

TABLE II
Gross Composition of Alberta Oil Sand Bitumens [5-7]
% of whole bitumen*

	Cold Lake	Athabasca	Peace River	Wabasca
Asphaltenes	15.3	16.9	19.8	18.6
Deasphalted oil	84	83.1	80.0	81.2
Acids	15.2	13.69	12.0	10.3
Bases	6.38	6.5	6.8	6.38
neutral N-compounds	1.15	1.35	1.41	2.67
Saturates	21.3	18.3	15.15	14.60
Monoaromatics	8.3	8.1	8.57	7.61
Diaromatics	3.6	3.8		
Polyaromatics+ non-defined polar compounds	24.35	23.8		
Thiopheno-aromatics from mono- and diaromatic fractions	0.8	0.88		

*Bitumen = 100%

As indicated by these data and the results of computerized gc-ms multiple ion cross scans [8] and matrix analyses, the bulk and fingerprint composition of these bitumens are quite similar and the minor differences which appear seem to signify some subtle trends in diagenetic history.

The similarity in chemical composition points to a common origin for the four major oil sand deposits. The distribution pattern of steranes (C₂₆, 5%; C₂₇, 44%; C₂₈, 33%; C₂₉, 17%; C₃₀, 1%) is reminiscent of the ratio obtained from the reduction of marine sterol mixtures and therefore suggests a marine origin. From microbiological model studies it can be concluded that AOSB is a microbiologically degraded residue. Microbiological simulation experiments showed that the end product of the microbiological degradation of a conventional oil is a bitumen-like material, low in paraffins and small ring, less alkylated aromatics and rich in polycondensed polyalkylated aromatics and polar materials, including asphaltene.

The Peace River and Athabasca bitumens seem to represent the end product of biodegradation. The Cold Lake bitumen contains slightly more paraffins, including small amounts of *n*-alkanes, and less asphaltene, and the Lloydminster heavy crude which is the least biodegraded material contains more paraffins and even less asphaltene.

The *n*-paraffins of the Cold Lake bitumen range from C₁₃ to C₃₃ with a maximum at C₁₉ and a carbon preference index of 1.0. The isoprenoid fraction contains both pristane and phytane along with lower and higher mw homologues of the series.

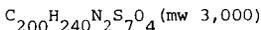
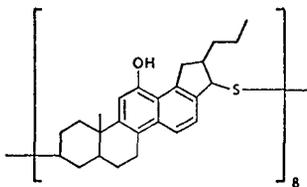
The gc-ms fingerprint spectra of the hopane series in all the oil sand bitumens showed the presence of the 17 α (H), 21 β isomer of C₂₇, C₂₉-C₃₅ hopanes with a maximum at C₃₀. Both C₂₂ diastereoisomers were present in approximately equal quantities. Living organisms synthesize the 17 β (H), 21 β isomer and the high conversion to the 17 α (H), 21 β isomer is indicative of some geothermal history of the oil sand, although the role of the mineral matter as a catalyst for the isomerization cannot be readily assessed.

Steranes and hopanes comprise only a small fraction of the saturates, the bulk of which still has not been identified. The compositions of the other separated fractions, the acids, bases, neutral nitrogen compounds, olefins, mono, di and polycycloaromatics, etc., are not well established either at present, although recent gc-ms multiple cross scan and matrix analyses have yielded valuable estimates.

As was pointed out above, the combined microbiological simulation and chemical analytical studies leave little doubt as to the severity of microbial degradation which the oil sand bitumen has suffered, nonetheless the question of whether the oil sand bitumen is a primary degraded kerogen without a significant thermal history, similar in character to the precursors of conventional oils, or whether it is the microbiological end product of a conventional oil has not been settled unambiguously.

The Chemistry of Bitumen Asphaltene.

The asphaltene fraction of the Athabasca bitumen has recently been subjected to detailed chemical studies for the elucidation of its molecular structure [9]. Here the essential question was to establish the role of sulfur in the polymeric framework of the asphaltene molecule. It was possible to show that in the Athabasca asphaltene the sulfur is present largely in the form of sulfides holding together dicycloaromatic carbon units of average molecular formula



Two of these molecules are joined together by hydrogen bonding. In reality, asphaltene is a complex mixture of molecules with a broad distribution of molecular weight and with significant deviations in the structures of monomeric units from the average dicycloaromatic unit above.

Esr studies of the Athabasca asphaltene showed the presence of paramagnetic species, approximately one free spin per 80-90 molecules and most of the molecules carrying free spin appear to carry more than one [10-12]. The resonance at $g=2.0036$ is thought to be associated with polycycloaromatic doublet radicals and singlet and triplet state diradicals. The relative distribution of these radicals can be influenced by temperature, the addition of paramagnetic gases such as O_2 and NO , and by other means. The effects are reversible. Since the minimum degree of condensation required in a cycloaromatic system for the formation of stable free radicals is about six, it seems that at least 1.1% of the asphaltene molecules contain at least one hexacycloaromatic sheet.

After completion of the initial phase of these studies on the molecular structure of the Athabasca asphaltene, current research has been extended in three directions:

a) It appeared to be desirable to compare the elemental composition, mw and the number of sulfide linkages in the polymeric framework of various asphaltenes from different sources. The results suggest that Athabasca asphaltene contains the highest percentage of bridged sulfur, as will be shown in a separate article [13,14].

b) More precise information on the chemical nature of the monomeric units liberated in the reductive cleavage of the sulfur-carbon bonds or in the mild thermolysis of the asphaltene will be obtained using a combination of hplc, gel permeation chromatography and organic geochemical microanalytical techniques.

c) Taking the synthetic approach, the feasibility of making asphaltene-like materials from simple or complex organic base materials by treatment with sulfur has been explored. In this way it was possible to prepare asphaltene-like materials with molecular weights approaching those of natural asphaltene in which the carbon monomeric units are joined together with sulfide linkages. Details of these studies will be given in another article [15].

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