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EFFECT OF BURIAL DEPTH ON THE HYDROCARBON-TYPE

DISTRIBUTION ON BITUMENS AND OILS FROM THE ALBERTA BASIN

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by

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ABSTRACT

A systematic study of hydrocarbon formation and conversion under the effects of maturation, especially geothermal maturation, can improve the reliability of the predictions associated with petroleum exploration and hence reduce the financial risk.

The hydrocarbon-type distribution (n-paraffins, saturated hydrocarbons, monoaromatics, diaromatics, polyaromatics, polar components and basic material) has been studied in four Cretaceous bitumens and crude oils of varying burial depths. Athabasca bitumen was subjected to thermal treatment of increasing severity, under reducing conditions to simulate the chemical effects of geothermal maturation. The generation and the change in relative distribution of various components due to this treatment were followed and compared with the effect of increasing burial depth.

Distillation, solvent deasphaltening and liquid chromatographic separations were applied in this study. Separation efficiency was monitored and components characterized by using refractive index and ultraviolet detectors, gas chromatography, mass spectrometry, ¹³C NMR and spectrofluorometry.

The simulated geothermal maturation produced chemical effects analogous to those attending increasing burial depth. A detailed study of the saturated bydrocarbons and polyaromatic fused-ring systems is also presented to confirm the same observation.

ii

INTRODUCTION

It is generally believed that the heavy oils in the lower Cretaceous reservoir rocks extending from west central Alberta through the Athabasca tar sands area into western Saskatchewan belong to a single oil system, which implies similar modes of origin (1). A current popular theory is that these bitumens and heavy oils are the biodegradation products of migrated conventional oils that have contacted meteoric water (2-4). Another theory advanced for the origin of the Athabasca tar sand is that "in-situ" precipitation and accumulation of humic acid during sand deposition (5) and a thin overburden caused transformation of the humate to immature petroleum. Others presented some evidence that the Athabasca Bitumen is young, not evaporated, altered or polymerized, (6,7).

In this study, we simulated the thermal maturation of Athabasca bitumen and followed the chemical changes during the reductive thermal treatments at increasing severities, to show that the chemical composition of the bitumen changes to resemble that of the more mature Cretaceous oils. The effects of geothermal maturation, as represented at various burial depths of oils, on the general hydrocarbon-type distribution has been investigated. A detailed study of the saturated hydrocarbons and polyaromatics is presented.

EXPERIMENTAL

Samples

-	The following nine samples were investigated:
1.	Athabasca bitumen separated by the hot water process at the Great
	Canadian Oil Sands (GCOS) plant (now Suncor).
2.	Cold Lake bitumen obtained by stream injection at 1500' (457 m)
	from the Manville Pool by Imperial Oil Co.
3.	Lloydminster oil produced by Husky OIl Co. from the Sparky
	Formation at 9A-3-50-1W4M, depth 1893' (577 m).
4.	Medicine River oil produced by Hudson Bay Oil and Gas Co. from
	the Glauconite zone, location 2-17-39-4W5M, depth 7326' (2233 m).

Five thermally hydrocracked products prepared from the above Athabasca bitumen.

The separation-characterization schematic diagram is shown in Fig. 1.

Reductive Thermal Treatment of Bitumen

The bitumen was treated under hydrocracking conditions of hydrogen pressure and temperature. The investigated samples were produced under increasing treatment severities represented by increasing pitch conversions.

Distillation and Deasphaltening

5.

All the samples were distilled up to 200° C and deasphaltened by precipitation in 20 volumes of pentane. The deasphaltened residues were vacuum distilled to 350° C, and the fraction boiling above 350° C was used for compound-type separation.

Compound-Type Separation

The deasphaltened distillation residues boiling above 200[°]C were separated into compound-type concentrates of saturates, monoaromatics, diaromatics, polyaromatics, polar compounds, and basic compounds on a dual-packed silica-alumina gel chromatographic column (9) and the polyaromatic concentrate was taken for further HPLC separation.

Analytical Methods Used

- <u>Fluorescent Indicator Absorption</u>: The light ends below 200^oC were analyzed for saturates, aromatic and olefinic contents by the FIA standard method (ASTM D1319-70).
- Optical Activity: The optical activities of the saturated hydrocarbons were determined by a "Model A" polarimeter, Bellingham and Stanley, Ltd.
- 3. <u>Gas Chromatography</u>: The fractions obtained from liquid chromatography were gas chromatographed on non-polar silicone rubber (SE 30) (5 ft. U-shaped glass columns, ¼ in 0.D.) to achieve separations according to boiling points. Normal alkanes were used as reference compounds. The column effluent was split between a flame ionization detector and a trapping out assmebly in a ratio of 1:9. Each collecting tube contained 10 mg of

chromosorb W. The column effluent could also be directed to a Dohrmann microcoulometric quantitative detector to determine the sulphur contents of the various peaks. Cuts were trapped out in the boiling range of C_{16} and C_{18} for the saturates in order to test for the presence of the isoprenoid hydrocarbons pristane and phytane. The aromatic fractions were cut to trap out major peaks in the chromatograms or regions in the area of the Kovat's indices of normal alkanes.

3

Rechromatography and Mass Spectrometry: The samples collected from simulated distillation were rechromatographed on lithium chloride coated silica. The column effluent was split between a flame ionization detector and a mass spectrometer in a ratio of 1:4. The mass spectrometer used was a C.E.C. 21-104 equipped with a Watson-Biemann type enriching device and operated at an ionization potential of 70 eV and with electric scan.

High Performance Liquid Chromatography (HPLC): The polynuclear 5. aromatic hydrocarbons were fractioned on a basis of number of fused aromatic rings by an HPLC system of diamine-silica using hexane/ methylene chloride mobile phase. The system was developed in our laboratory (10,11).

GC/MS Analysis of PNAs: A Finnegan Model 4000 GC-MS system employing electron impact at 70 eV (scan time 0.3 sec/500 a.m.u.) direct inlet to mass spectrometer and a data acquisition Ingos Nova I computer was used for HPLC cut characterization. Concentrated aromatic sub-fractions were separated on a glass column (1.8 m x 6.3 mm o.d., 2 mm i.d.) packed with 2.5% Dexil 300 on (80-100 mesh) chromosorb W, A.W. and helium was used as carrier gas (25 cm³/min). Samples were injected at 220 $^{\circ}$ C and a temperature program of 10 $^{\circ}$ /min was used from 100 to 300°C.

Nuclear Magnetic Resonance Spectometry: Samples for ¹³C NMR analyses were weighed directly into 5-mm NMR tubes. Deuterochloroform (CDCL₂) was added as solvent reference and internal lock. Chromium (tris) acetylacetonate $(Cr(ACAC)_3)$ was added to the sample so that a r pid pulse repetition rate could be used without severe line broadening or shifting. The analysis was performed on a Varian

4.

6.

7.

CFT-20 Fourier transform.

8.

<u>Spectrofluorimetry</u>: Fluorescence excitation and emission spectra, uncorrected for variation of source and photomultiplier response, were recorded in HPLC grade hexane dried with activated molecular sieves. A Varian SF330 spectrofluorimeter was used. The spectra were recorded in dilute solutions to avoid excimer formation. Appropriate cut-off filters were used in the emission beam. Each sample was irradiated at several different wavelengths to obtain optimum emission spectra. Similarly, excitation spectra were recorded with the emission monochromator set at different wavelengths. <u>Elemental Analysis</u>: Elemental analysis of the PAH fractions of both oils, obtained from the silica-alumina chromatographic separation, was performed on a Perkin Elmer 240 Analyzer.

9.

RESULTS and DISCUSSION

Boiling Point Distribution

The distillation yields and sulphur contents of the four oils are shown in Table 1. If the proportion of light ends is considered to be an indication of the extent of thermal maturation of an oil, it can be seen that the Athabasca oil would be the least mature and the Medicine River the most thermally mature. Table 2 shows that hydrocracking of bitumen produces the same effect on the products. The increase in the severity of cracking increasing the lighter ends at the expense of the residual fractions and asphaltenes.

Hydrocarbon-Type Distribution

When the compound-type distributions in the cretaceous oils are compared with those of the hydrocracked Athabasca (Tables 3,4) similar trends are observed. Increased in the saturated hydrocarbons class are additions caused by the cleavage of side chains from the asphaltenes. The large increase in the monochromatic weight percent could also be explained by the hydropyrolysis and cleavage from the asphaltenes. The latter decreased considerably under the effect of both geothermal maturation as well as hydrocracking in the laboratory. The polyaromatics, polar and basic compounds decrease substantially.

Saturated Hydrocarbons

The simulated distillation chromatograms of the saturates are shown in Figures 2-5. The predominant peaks in Medicine River saturates are normal alkanes as expected for an undergraded thermally mature oil. The chromatograms from the other oils show no predominant normal alkanes. All oils show maxima in the region of normal C_{17} . Also it should be noted that both the Athabasca and Lloydminster fractions show substantial amounts of material in the C_{27} to C_{29} range in which steranes are expected. Of course some of this material would be in the next distillate fraction.

Normal alkanes to isoprenoid ratios are often used as indicators of the extent of biodegradation of oils. Therefore cuts were trapped out from the simulated distillates in the boiling range of $C_{17} - C_{18}$ normal

alkanes and rechromatographed on lithium chloride coated silica. During the rechromatographic separations cyclic materials are eluted before the noncyclic saturates. In the Medicine River cuts, Figures 7, and 8, the normal C_{17} and normal C_{18} are more prominent than the corresponding isoprenoid hydrocarbons pristane and phytane. This would be interpreted to be a thermally undegraded oil for according to the work of Tissot *et al.*, (3) 1971 in the investigation of the processes of maturation in oils from the Lower Toarcian Paris basin, the isoprenoids are dominant during early stages but the normal alkanes become dominant later during maturation.

The rechromatograms of the corresponding simulated distillation cuts from the Lloydminster are shown in Figures 9 and 10. The normal C_{17} and C_{18} contents are much lower than those of the pristane and phytane. This can be explained by immaturity as well as biological degradation or by both factors. Possibly the source material also influences the contents of normal alkanes and isoprenoids that are derived from it. Figure 6 shows the Pristane and Phytane chromatograms for the various oils.

Cyclic Alkanes

A comparison of the cyclic material in Medicine River, LLoydminster and Athabasca saturated hydrocarbons in the C_{19} to C_{25} range is shown in Table 5.

In this table only the cyclic material is discussed which constitutes a small portion of the Medicine River saturates but a major portion of the heavy oils. The main cyclic material in the Medicine River saturates in this molecular weight range consists of mono, di and tricyclic compounds. The Lloydminster contains only half the amount of monocyclics as the Medicine River and the Athabasca has almost no monocyclic material. The Athabasca saturates are the most highly cyclized saturates, folowed by the Lloydminster with the Medicine River saturates containing the least highly cyclized material.

The lower content of monocyclics in the heavy oils might be explained on the basis of biological degradation. On the other hand, these heavy oils, in particular the Athabasca, might never have had much of this material or it might have become aromatized. The fact that the saturated fractions of Athabasca and Lloydminster oils contain a greater proportion of tri- and tetracyclic compounds than the Medicine River saturates could be interpreted

as an indication that they are less mature with the Athabasca being the lease mature.

The same effect is produced by hydrocracking Athabasca bitumen (Table 6).

Optical Activity of Saturated Hydrocarbons.

The optical activity (degree of rotation) obtained per gram of saturated hydrocarbons from the gas-oil fractions of the various oils is shown in Table 7. It can be seen that the optical activity of the saturated hydrocarbons from the gas oils of the Medicine River oil is the lowest. That of the Lloydminster oil it is about four times as great, while of both the Cold Lake and Athabasca oils the optical activity is about five times that of the Medicine River oil The saturated fraction of the total Athabasca bitumen has the highest value, indicating that the optical activity is greatest in the higher-molecular-weight saturates, where it would be expected that the components have undergone minimal changes from the structures of the original biological precursors.

According to Silverman (12) the material that is the least mature would consequently be the most optically active. On this basis it seems that, as expected, the medicine River oil is the most mature and the Athabasca and Cold Lake oils are the least.

Polynuclear Aromatics

The total polyaromatic content in the deasphaltened oils decreases considerably (20.1% to 8.6%) with increasing burial depth of the hydrocarbon pool (Table 3). PAH diminution under increasing severity of thermal conditions is caused by increasing loss of aliphatic substitution, while aromaticity actually increases, as will be seen later.

We have discussed in detail the effect of burial depth on the distribution of the hydrocarbon class in a previous publication (13). Also the distribution of fused aromatic ring number for naturally maturing as well as processed samples was investigated (Table 8). The 3-ring components, phenanthrenes and anthracenes increase gradually with increasing burial depth. The 4-ring aromatics pyrenes and chrysenes also show the same trend, but to a lesser degree. These increases seem to take place at the expense of PAHs containing more than 4 fused rings per molecule, i.e.,

benzo [a] pyrenes, perylenes and dibenzo[a,h] anthracenes, which decrease from 25% to 15% with increasing depth. These results have been qualitatively verified by the fluorescence excitation and emission spectra, and quantitated using the refractive index detector. The strong retention of some of the PAH material on the diamine column so that they could not be recovered by the mobile phase does not lessen the validity of the above observations.

Increase of the 3- and 4-ring molecules at the expense of the higher ring number aromatics resembles hydrocracking effects that cause ring rupture, usually preceded by a saturation step.

Analysis with ¹³C nuclear magnetic resonance revealed that as the thermal conditions become more severe these aromatic molecules become increasingly aromatic in character through depletion of the number and length of the aliphatic substituents on the aromatics. This effect was simulated successfully by hydrocracking Athabasca bitumen (Table 8). An operational factor that could contribute to the diminution of the aromatics containing more than four aromatic rings is that with increasing maturity these compounds tend to be dealkylated and therefore precipitated more effectively by the pentane in the asphaltene precipitation step and thus removed from the system being analyzed.

CONCLUSION

Studying the effects of increasing geothermal maturation on the chemical structure of various component is effective to assess their potential as "maturity indices" for improved prediction of the thermal maturity status needed for the correlation of oils. Increasing burial depth of pooled hydrocarbons exerted considerable chemical conversion trends on their class distribution particularly in the saturated and polyaromatic hydrocarbons.

REFERENCES

- 1. Vigrass, L.W., "Geology of Canadian Heavy Oil Sands", Ama Assoc. Petroleum Geologists Bull., <u>52</u>, 1984 (1968).
- 2. Bailey, N.J.L., Jobson, A.M. and Rogers, M.A., "Bacterial degradation of Crude Oils", Chem. Geol., 11, 203-221 (1973).
- Krouse, H.R., Evans, C.R., and Rogers, M.A., "Alteration of Crude Oil by Water and Bacteria", Am. Assoc. Petroleum Geologists Bull., <u>57</u> 126, (1973).
- 4. Evans, C.R., Rogers, M.A. and Bailey, N.J.L. "Evoluation of Petroleum in Western Canada" Chem. Geol., 8, 147-170 (1971).
- 5. Corbett, C.S. "In-Situ Origin of McMurray Oil in Northeastern Alberta and its Relevance to the General Problem of Origin of Oil", Amer. Assoc. Petrol. Geologists Bull., <u>39</u>, 1601-1621 (1955).
- 6. Montgomergy, D.S., "On the Origin of Athabasca Oil", Athabasca Oil Sands Conf. Proc., 55-65 (1951).
- Montgomery, D.S., Banerjee, R.C. and Sawatzky, H., "Optical Activity of the Saturated Hydrocarbon from the Alberta Heavy Cretaceous Oils", Bull Canada Petrol. Society, 22 No. 3, 357-360 (1974).
- 8. Tissot, B., Caliget-Debyser, Y., Deroo, G., and Oudin, J.L. "Origin and Evolution of Hydrocarbons in Early Toarcian Shales", Am. Assoc. Petroleum Geoligists Bull., 55, 2177 (1971).
- 9. Sawatzky, H., George, A.E., Smiley, G.T. "Fuel", 55, 16 (1976).
- 10. Chmielowiec, J. and George, A.E., Anal. Chem. 52, 1154-1157 (1980).
- 11. Chmielowiec, J., Beshai, J.E. and George, A.E. "Fuel", 59, 838-844 (1980).
- 12. Silverman, S.R. "Infuence of Petroleum Origin and Transformation on its Distribution and Redistribution in Sedimentary Rocks", Proc. 8th World Petroleum Congress, Vol 2, p. 47-54 (1971).
- 13. George, A.E., and Beshai, J.E., "Effects of Burial Depths on the Distribution of Polynuclear Aromatics in Bitumens and Oils of the Alberta Basin", Preprints Division of Pet. Chemistry, ACS National Meeting, N.Y., Aug. 24-29, 1981.

DISTILLATE YIELDS AND THEIR SULPHUR CONTENTS

	ATHABASCA	COLD LAKE	LLOYDMINSTER	MED. RIVER
Light ends, wt %	4.5	5.9	12.5	44.8
Distillate, wt %	37.5	31.0	36.0	43.5
Distillate Sulphur, wt %	2.90	2.85	2.50	0.80

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TABLE 2

GROSS COMPOSITION OF ATHABASCA BITUMEN AND PRODUCTS OF HYDROCRACKING

SAMPLE	PITCH CONVERSION 	GAS	<u>NAPHTHA<200⁰C</u>	MALTENES>200 ⁰ C	ASPHALTENES
1	59.1	3.9	7.0	75.7	13.4
2	68.9	4.0	11.5	72.2	12.3
3	77.4	5.9	13.1	70.5	10.5
4	80.0	6.8	13.5	72.7	7.0
[`] 5	91.4	9.2	18.5	69.6	2.7

	UMPOUND-TIPE	DISIRIBUI	TONA IN	BI10ME	NB	
	AND OIL	S OF ALBE	RTA BAS	IN		
			wt%			
SAMPLE	SATURATES	MA	DA	PA	PM	BM

Athabasca	21.0	7.8	11.0	20.1	19.0	5.7
Cold Lake	22.1	13.8	9.1	14.5	16.6	4.8
Lloydminster	31.3	16.2	7.2	11.3	13.5	3.2
Medicine River	57.5	18.0	5.7	8.6	9.2	0.9
 MA - monoaromatics*	5	DA - diar	omatics			PA - pol
PM - polar materia	al	BM - basi	c mater	ial		•

TABLE 4

EFFECT OF HYDROCRACKING ON COMPOUND-TYPE DISTRIBUTION

				wt %			
SAMPLE	SATURATES	MONONUCLEAR AROMATICS	DINUCLEAR AROMATICS	POLYNUCLEAR AROMATICS	POLAR COMPOUNDS	BASIC COMPOUNDS	ASPHALTENES
Feed	21.0	7.8	11.0	20.1	19.0	5.7	15.3
1	33.4	9.3	10.5	14.2	12.8	2.3	13.4
2	36.1	10.1	10.7	12.9	11.6	2.1	12.3
3	3 8.9	10.5	11.0	11.7	9.8	1.6	10.5
4	42.5	10.5	10.1	1 1.1	10.5	1.2	7.0
5	47.8	11.5	9.7	9.1	8.8	0.9	2.7

11

C 100 10 17 10 17 100 17

A - polyaromatics

TO C ₂₅ RANGE				
	Medicine River	Lloydminster	Athabasca	
, %	25	13	trace	
7	33	35 ·	31	
7.	33	30	44	
c, %	7	22	25	
c, %	-	trace	trace	
	, % % % 2, % 2, %	TO C ₂₅ RANGE <u>Medicine River</u> , % 25 % 33 % 33 % 33 2, % 7 c, % -	TO C ₂₅ RANGE Medicine River Lloydminster , % 25 13 % 33 35 % 33 30 2, % 7 22 c, % - trace	

 TABLE 6
 - THE EFFECT OF THERMAL HYDROCRACKING ON THE APPROXIMATE COMPOSITION

 OF CYCLIC SATURATES OF ATHABASCA HEAVY OIL PRODUCT

· · · · · · · · · · · · · · · · · · ·	·····		
	Percentage		
· ·	Feed	Product	
Acyclics	trace	considerable	
Monocyclics	trace	10	
Dicyclics	30	40	
Tricyclics	30	40	
Tetracyclics	30	10	
Penta- to Heptacyclics	. 10	trace	

1)

OPTICAL ROTATIONS PER GRAM OF SATURATED HYDROCARBON

SOURCE	UNDILUTED SAMPLE	SAMPLE IN 20% BENZENE SOLUTION
Medicine River gas oil		$+0.048^{\circ} \pm 0.002^{\circ}$
Lloydminster gas oil	$+0.157^{\circ} \pm 0.006^{\circ}$	$+0.190^{\circ} \pm 0.001^{\circ}$
Cold Lake gas oil	$+0.259^{\circ} \pm 0.001^{\circ}$	$+0.239^{\circ} \pm 0.005^{\circ}$
Athabasca gas oil	$+0.217^{\circ} \pm 0.005^{\circ}$	$+0.242^{\circ} \pm 0.008^{\circ}$
Athabasca total bitumen	$+0.314^{\circ} \pm 0.002^{\circ}$	$+0.335^{\circ} \pm 0.004^{\circ}$

	Athabasca	Cold Lake	Lloydminster	Medicine River	Processed Athabasca	
3-ring	37	40	48	49	52	
4-ring	21	23	23	25	[.] 27	
>4-ring	25	21	19	15	13	
retained on column	17	16	10	11	8	
Model compounds used to determine calibration factors: 3-ring - phenanthrene, anthracene 4-ring - pyrene, chrysene >4-ring - dibenzo[a,c]anthracene						

Quantitative Distribution of Aromatic Ring Classes Using Refractive Index Detector (wt % of the total PAH fraction in deasphaltened residue boiling above 350°C)



FIGURE 1: Separation and Characterization Schematic



Fig. 2 Athabasca saturates SE-30 on Chromosorb W.



Fig 4 Lloydminster saturates SE-30 on Chromosorb W.



Fig. 3 Cold Lake saturates SE-30 on Chromosorb W.



Fig. 5 Medicine River saturates SE-30 on Chromosorb W.

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Fig. 6 Gas Chromatograms of nC₁₇ - Pristane, nC₁₈ - Phytane (on CiCl chromosorb A).

