

INVESTIGATION OF POSSIBLE ROUTES  
TO ASPHALTENE IN NATURE

A.V. Kemp-Jones and O.P. Strausz  
Hydrocarbon Research Center  
Department of Chemistry, University of Alberta  
Edmonton, Alberta, Canada, T6G 2G2

INTRODUCTION

The literature contains relatively little evidence to indicate how asphaltene is formed in nature. In particular the frequent proposals of an asphaltene structure consisting of polynuclear aromatic sheets (1,2,3) have not been accompanied by suggestions as to what chemical reactions might produce such structures. Knowing how asphaltene is formed in nature might provide some indication of how to reverse the process.

We have proposed the average structure I for Athabasca asphaltene on the basis of a detailed chemical and spectroscopic study (4). A possible route to such a structure is the aromatization and condensation of smaller molecules of biological origin with sulfur and/or hydrogen sulfide. Hydrogen sulfide is produced in nature by sulfate-reducing bacteria, which often use petroleum as the energy source (5). Heating terpenes with sulfur or selenium at high temperatures to convert them to more readily identifiable aromatic hydrocarbons is a well-established method in structure elucidation. Heating cholesterol with selenium produces the Diels hydrocarbon, methylcyclopentanophenanthrene, which was found in petroleum by Mair. Mair has noted the general similarity between the structure of certain petroleum hydrocarbons and those produced by heating terpenes with sulfur (6). In one experiment Douglas and Mair reported heating cholesterol with sulfur and obtaining "petroleum-type hydrocarbons" (7). They also reported obtaining dark viscous materials with high sulfur content. We have carried out similar experiments to determine whether asphaltene is formed under these conditions.

EXPERIMENTAL

Reaction of Cholesterol with Sulfur

Powdered cholesterol (40 g), sulfur (20 g) and, in most experiments, clay (20 g) were shaken until thoroughly mixed and then heated under nitrogen at 170° for 7 days. The mixture was cooled, diluted with benzene (about 3:1) until mobile and centrifuged to remove the clay. The benzene solution was shaken overnight with mercury and centrifuged to remove mercury sulfide, if any, and mercury. Excess mercury was always present. The benzene solution was concentrated to a benzene:product ratio of 1:1 and diluted with 60 volumes of n-pentane. The material which precipitated was collected by filtration, washed with n-pentane, and then Soxhlet extracted for three days with ether. The residual solid was dried at 50°C and <1mm Hg for two days. Typical analysis: C, 74.0; H, 7.7; S, 17.0; O, 1.3.

Reaction of Dimethylnaphthalene with Sulfur

Technical grade dimethylnaphthalene from Terochem Laboratories, Edmonton, was used. It was completely soluble in pentane and had the correct carbon and hydrogen analysis but contained 0.3% nitrogen. The dimethylnaphthalene (200 g, 1.28 moles) and powdered sulfur (17.2 g, 0.54 mole) were heated at 140° for 3 days while exposed to the air. The product was diluted with benzene and the insoluble material ("coke") was filtered off (10.25 g). The total volume was reduced to 400 ml and the mixture was diluted with 6 l. of pentane. The precipitate was

collected and boiled with 10% aqueous sodium sulfite containing a few drops of ethanol for 4 hours to remove sulfur. The residue was extracted with benzene, dried, filtered and the benzene evaporated to leave the product (3.95 g, 2% yield). Analysis: C, 80.5; H, 5.0; N, 1.4; S, 10.7; O, 2.4.

#### Reaction of Maltenes with Sulfur

The maltenes from Athabasca bitumen (33.9 g) and sulfur (1.7 g) were stirred mechanically in a 200 ml flask with reflux condenser under nitrogen for 1 hour, then heated to 170° for 20 hours. The mixture was diluted with benzene, in which it was completely soluble, and shaken overnight with mercury. The solution was decanted and diluted with pentane to precipitate the product, which was Soxhlet extracted with pentane and dried. Yield 0.84 g. Analysis, after correcting for 1.9% ash, C, 79.7; H, 7.9; N, 1.0; S, 9.4; O, 2.1. MW 7813.

#### Reduction of Synthetic Asphaltene with Lithium Aluminum Hydride

1 g of synthetic asphaltene, containing 5 mg-atoms of sulfur, was added to a solution of 7 mmoles of lithium aluminum hydride in 27 mls of tetrahydrofuran. The mixture was stirred under nitrogen at room temperature for 5 hours and then refluxed for 16 hours. After cooling, 9% HCl was added, cautiously at first, until the inorganic material separated as a white paste. The solution was decanted, rinsing the paste with dichloromethane. The solvent was evaporated, the residue was dissolved in dichloromethane and washed with 9% HCl. The dichloromethane was evaporated and the residue redissolved in 25 mls of tetrahydrofuran. A solution of KOH (350 mg, 3 pellets) in 5 ml of 98% ethanol was added. After stirring 10 minutes, 1.25 mls of octyl iodide was added and the mixture was stirred overnight. Most of the solvent was evaporated and the residue was partitioned between dichloromethane and 9% HCl. The dichloromethane was evaporated and the residue was pumped at 50°C and 0.1 mm Hg under a dry-ice/acetone cold finger to remove most of the octyl iodide. GC analysis with hexadecane as internal standard showed that the product contained 3.12% of octyl iodide. Recovered 1.04 g. Analysis, corrected for 2.8% ash, C, 77.1; H, 9.3; O, 1.5; S, 12.1. MW, found 974, after correcting for octyl iodide present 1129, after correcting for octyl groups added 952.

### RESULTS AND DISCUSSION

Our first attempt to prepare a synthetic asphaltene involved heating dimethylnaphthalene with sulfur. The major part of the pentane-insoluble product was also insoluble in benzene ("coke"), but a small yield of benzene-soluble material was also obtained. This asphaltene was quite different from natural asphaltene, having a molecular weight of only 486, an H/C ratio of 0.78, and a sulfur content of 11%. The H nmr spectrum was also completely different from that of Athabasca asphaltene.

However a material strikingly similar to natural asphaltene can be obtained by heating cholesterol with sulfur. The yield of synthetic asphaltene obtained under various conditions, together with the number average molecular weight, H/C ratio and sulfur content are shown in the Table. The yield of asphaltene is substantially increased when clay is present. Preliminary experiments suggest that kaolin is more effective than montmorillonite, contrary to expectation. The number average molecular weight of the synthetic asphaltene is about 2000, whereas that of Athabasca asphaltene is 3000 after allowing for hydrogen bonding. The H/C ratio has been reduced from 1.7 in the starting material, cholesterol, to an average of 1.25 which compares with 1.19 for Athabasca asphaltene and an average of 1.16 for 33 analyzed samples in the literature (8). The major difference between the synthetic and natural asphaltene is that the synthetic asphaltene contains an average of 17% sulfur while the highest value recorded for a natural asphaltene is 9.6% (8b). Attempts to obtain an asphaltene with lower sulfur content from cholesterol were not successful. When the amount of sulfur

TABLE  
 Reactions of Cholesterol (40 g) with Sulfur  
 Under Various Conditions

Reaction Conditions				Yield(g)	MW	% S	H/C
Sulfur(g)	Clay(g)	Temp.(°C)	Time (days)				
20	20	170	7	9.5	1905	17.0	1.24
20	20	170	7	8.4	2093	17.0	1.24
			Average	9.0	1999	17.0	1.24
15	20	170	7	1.3	2060	16.9	1.27
15	20	170	7	2.0	1809	15.9	1.26
15	20	170	7	1.1	1904	16.4	1.25
			Average	1.5	1924	16.4	1.26
20	0	170	7	3.6	1631	19.0	1.27
20	20	150	30	3.7	1893	24.2	1.37

was reduced to 10 g (with 40 g of cholesterol), no asphaltene was produced. If the amount of sulfur was reduced to 15 g, the yield of asphaltene dropped substantially, but the sulfur content decreased only slightly from an average of 17.0% to 16.4%, barely outside the experimental variance. The high sulfur content, roughly twice that of natural asphaltene, suggested that disulfide groups might be present. To test this possibility the synthetic asphaltene was treated with lithium aluminum hydride which would reductively cleave any disulfide groups to thiols (9) and cause a decrease in the molecular weight, if the disulfide group is not in a ring. The product was alkylated with octyl iodide to protect any thiol groups generated. This procedure caused a decrease in the molecular weight from 1905 to 952, after allowing for the weight of the octyl groups added (3.1 per molecule), showing that only one disulfide group per molecule is present. Addition of three octyl groups implies that no more than three thiol groups were generated, which corresponds fairly well to the two thiol groups expected from cleavage of one disulfide bond, and shows that there are few if any disulfide groups in rings. Reduction of the synthetic asphaltene with potassium and naphthalene in tetrahydrofuran, which cleaves carbon-sulfur bonds (4), decreased the molecular weight to 416, very close to the cholesterol molecular weight of 387. This shows that the polymer is held together by sulfide bridges, rather than by carbon-carbon bonds. 4.6 sulfur atoms per molecule must be involved in such bridges, with one a disulfide bridge, to cause the observed decrease in molecular weight, so that the remaining 5.5 sulfur atoms per molecule may be in rings.

The IR, NMR and UV spectrum of the synthetic asphaltene are quite similar to those of Athabasca asphaltene, as shown in the Figures. The <sup>1</sup>H NMR spectrum of the synthetic asphaltene shows that 6% of the hydrogen atoms are aromatic, quite close to the 8% found for Athabasca asphaltene. The <sup>13</sup>C NMR spectrum of the synthetic asphaltene shows that 32% of the carbon atoms are aromatic compared to 42% for Athabasca asphaltene. These figures are consistent with the slightly higher H/C ratio for the synthetic asphaltene. A difference between the synthetic and Athabasca asphaltene is apparent when the <sup>1</sup>H NMR spectrum is arbitrarily divided into "benzylic", "saturated CH<sub>2</sub>", and "saturated CH<sub>3</sub>" regions at δ4.50-1.75 for "benzylic", δ1.75-1.05 for "saturated CH<sub>2</sub>" and δ1.05-0.0 for "saturated methyl". (The spectrum does show minima at about δ1.05 and 4.50 but not at δ1.75). The three regions are in the ratio 0.72:1:0.54 for Athabasca asphaltene and 0.82:1.0:0.90 for the synthetic asphaltene, i.e. there appears to be more "saturated methyl" absorption in the synthetic asphaltene. The synthetic asphalt-

tene also shows an intense EPR signal similar to the main peak in the spectrum of Athabasca asphaltene.

In view of the high sulfur content of the asphaltene produced by heating cholesterol with sulfur, we have investigated the properties of the asphaltene produced by heating the Athabasca maltene with sulfur under the conditions reported by Bestougeff for Hassi-Messaoud maltene (10). The asphaltene produced in this way had an average molecular weight of 7813, 9.4% sulfur and an H/C ratio of 1.18. These values are very close to those of Athabasca asphaltene. Apparently there are some molecules present in the maltene which can be polymerized by sulfur without incorporating sulfur into the units of the polymer. These molecules are probably in the resins, where the molecules with reactive functional groups are concentrated. Since little is known about the structure of the molecules in the resins, we do not know what kind of molecules are responsible. However the experiment provides further support for the suggestion that polymerization of smaller molecules with sulfur is a possible route to asphaltene in nature.

#### CONCLUSIONS

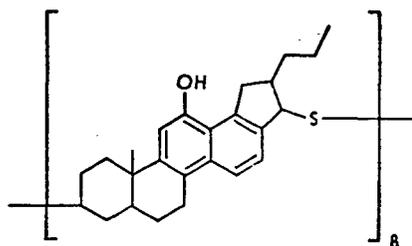
Reaction of cholesterol with sulfur produces material very similar to natural asphaltene. The synthetic asphaltene consists of small units held together by sulfur bridges, as was previously found for Athabasca asphaltene. Reactions of this type are a reasonable route to asphaltene in nature, and are the only route supported by experimental evidence.

#### ACKNOWLEDGEMENTS

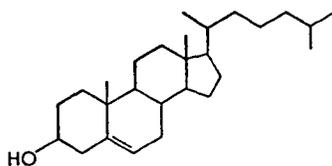
We are grateful to the National Research Council for financial support, and to the Alberta Oil Sands Technology Research Authority for a fellowship to one of us (A.V. K-J.). Mr. Cleve Murray provided technical assistance.

#### REFERENCES

- (1) Yen, T.F., *Energy Sources*, 1, 447 (1974).
- (2) (a) Erdman, J.G., *Adv. Org. Geochem.*, 215 (1964).  
(b) idem, "Hydrocarbon Analysis", ASTM Spec. Tech. Publ. 389, 259 (1965).
- (3) Speight, J.G., *Fuel*, 50, 102 (1971).
- (4) Ignasiak, T., Kemp-Jones, A.V., and Strausz, O.P., *J. Org. Chem.*, 42, 312 (1977).
- (5) (a) Kuznetsov, S.I., Ivanov, M.V., and Lyalikova, N.N., "Introduction to Geological Microbiology", McGraw-Hill, New York, 1963.  
(b) Davis, J.B., "Petroleum Microbiology", Elsevier, Amsterdam, 1967.
- (6) Mair, B.J., *Geochim. Cosmochim. Acta*, 28, 1303 (1964).
- (7) Douglas, A.G., and Mair, B.J., *Science*, 499 (1965).
- (8) (a) Erdman, J.G., and Ramsey, V.G., *Geochim. Cosmochim. Acta*, 25, 175 (1961).  
(b) Padovani, C., Berti, V., and Pinetti, A., *Proc. 5th World Pet. Congr.*, Sec. V, 273 (1959).  
(c) Koots, J.A., and Speight, J.G., *Fuel*, 54, 179 (1975).
- (9) Arnold, R.C., Lien, A.P., and Alm, R.M., *J. Am. Chem. Soc.*, 72, 731 (1950).
- (10) (a) Bestougeff, M., *Bull. Soc. Chim. Fr.*, 4773 (1967).  
(b) idem, *Proc. 7th World Pet. Congr.*, 9, 129 (1969).



I



Cholesterol

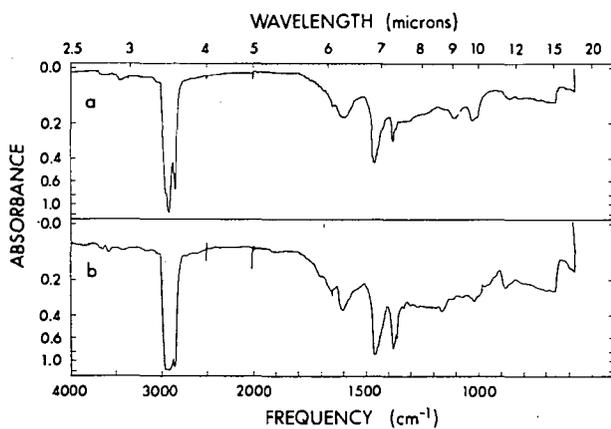


Figure 1. (a) IR spectrum of Athabasca asphaltene (2.7% in  $\text{CHCl}_3$ ).  
 (b) IR spectrum of synthetic asphaltene prepared from cholesterol and sulfur (2.7% in  $\text{CHCl}_3$ ).

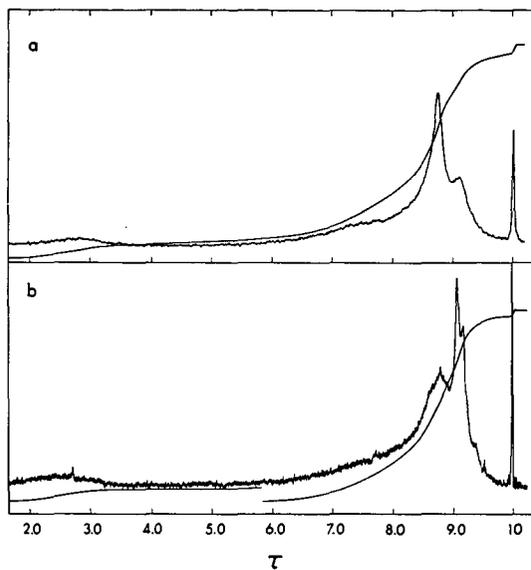


Figure 2. (a)  $^1\text{H}$  NMR spectrum of Athabasca asphaltene.  
 (b)  $^1\text{H}$  NMR spectrum of synthetic asphaltene prepared from cholesterol and sulfur.

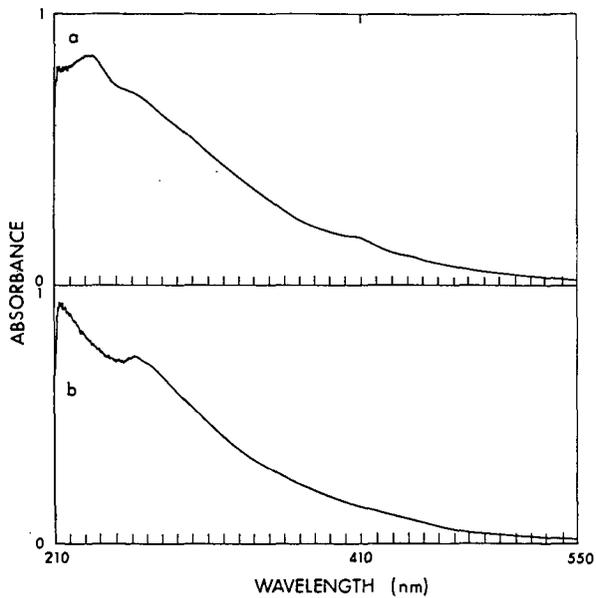
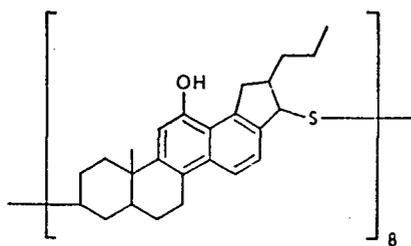
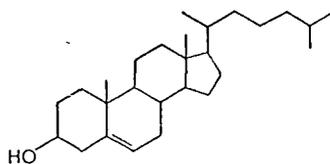


Figure 3. (a) UV spectrum of Athabasca asphaltene (16 mg/l in tetrahydrofuran).  
 (b) UV spectrum of synthetic asphaltene prepared from cholesterol and sulfur (15 mg/l in tetrahydrofuran).



I



Cholesterol

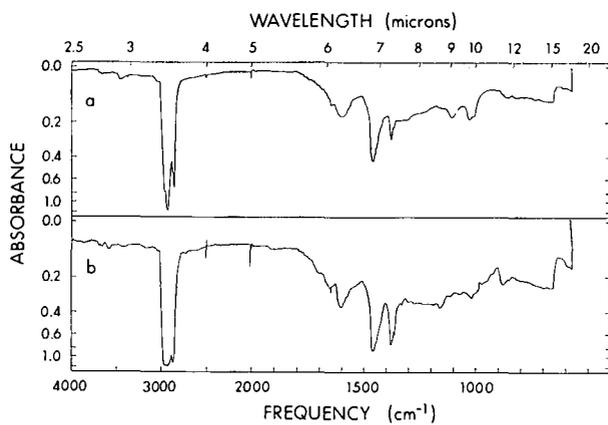


Figure 1. (a) IR spectrum of Athabasca asphaltene (2.7% in  $\text{CHCl}_3$ ).  
 (b) IR spectrum of synthetic asphaltene prepared from cholesterol and sulfur (2.7% in  $\text{CHCl}_3$ ).

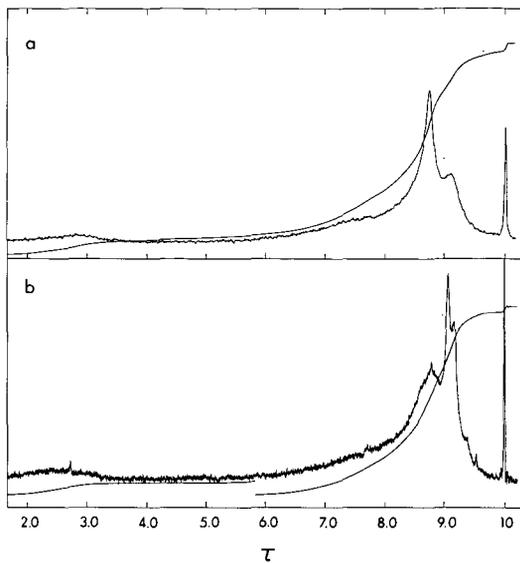


Figure 2. (a)  $^1\text{H}$  NMR spectrum of Athabasca asphaltene.  
 (b)  $^1\text{H}$  NMR spectrum of synthetic asphaltene prepared from cholesterol and sulfur.

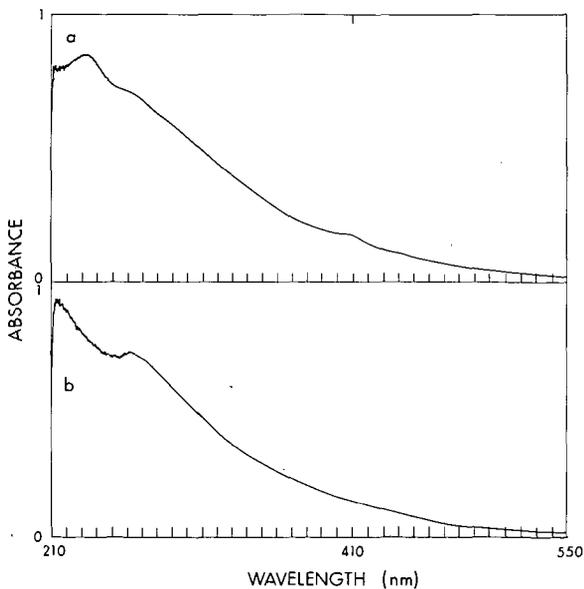


Figure 3. (a) UV spectrum of Athabasca asphaltene (16 mg/l in tetrahydrofuran).  
 (b) UV spectrum of synthetic asphaltene prepared from cholesterol and sulfur (15 mg/l in tetrahydrofuran).

## CHEMICAL CHANGES DURING THERMAL HYDROCRACKING OF ATHABASCA BITUMEN

A.E. George, G.T. Smiley and H. Sawatzky

Canadian Fossil Fuel Research Laboratory,  
Research on Bituminous Substances Section,  
Energy Research Laboratories, CANMET,  
Department of Energy, Mines and Resources,  
Ottawa, Canada.

### INTRODUCTION

Non-catalytic thermal hydrocracking is a method of upgrading Athabasca bitumen. It reduces or eliminates waste coke production and, if combined with gasification of the residue, is less polluting than the currently used coking processes. In a previous report (1) we described some of the chemical conversions that take place during the hydrocracking of the bitumen. The work described here is a continuation of the previous studies on the hydrocracked products.

### EXPERIMENTAL

A schematic diagram of the procedure and the breakdown to compound-types is shown in Figure 1.

#### Samples:

1. Athabasca bitumen obtained from the Great Canadian Oil Sands' hot water separation process.
2. Five samples of hydrocracked bitumen, selected to represent increasing severities of treatment as expressed in pitch conversion to distillable fractions.

#### Thermal Hydrocracking

The hydrocracking pilot plant and its operation have been described in a previous report (2) by our colleagues in the Process Engineering Section of the Canadian Fossil Fuel Research Laboratory of the Energy Research Laboratories. Athabasca bitumen and hydrogen are fed at the bottom. The resulting products, both liquid and vapour, flow from the top of the reactor to a hot separator. The condensed material in this receiver is withdrawn continuously as a heavy oil product (HOP) through a pressure reducing valve into an atmospheric receiver. The uncondensed vapours flow from the hot separator to a cold receiver where the light oil product (LOP) is withdrawn continuously. The gas stream from the cold receiver, consisting mainly of hydrogen and containing impurities such as uncondensed hydrocarbon gas, hydrogen sulphide and ammonia, is oil-scrubbed. The scrubbed hydrogen is joined by fresh make-up hydrogen and is then recycled to the reactor at a constant controlled rate. Five liquid samples of both the light and heavy oil products representing increasing degrees of hydrocracking were selected for investigation. Three of these samples are representative of steady state conditions at a liquid hourly space velocity of 2 and temperatures of 435, 445 and 455°C. Similarly, the other two samples were obtained at a liquid hourly space velocity of 1 and temperatures of 445 and 460°C. All the samples resulted from processing at 2000 psi operating pressure and a hydrogen recycle rate of 1.5 cu ft/hr. at the same operating pressure and a temperature of 25°C. The hydrogen purity was 85%. The distribution of product between light and heavy oil depends on the hot-receiver temperature, the gas/liquid ratio entering the receiver, and the degree of cracking to which the product is subjected (3).