

Distillation

Light oil product (LOP) was separated by distillation (ASTM D216-54) to light ends boiling below 200°C and a fraction boiling above 200°C. The heavy oil product (HOP) did not contain any light ends boiling below 200°C. The distillation residue of the HOP boiling above 524°C under atmospheric pressure is defined as pitch.

Deasphalting

The asphaltene portion of the heavy oil (HOP) was precipitated by the addition of twenty volumes of pentane to one volume of oil. The asphaltenes were separated by filtration, extracted with pentane in a Soxhlet Extractor and dried first on a water bath and then under reduced pressure at 50°C. The main pentane solubles and washings were combined and n-pentane was completely evaporated from these maltenes.

Compound-Type Separation

The light ends distilling below 200°C were analysed for saturate, aromatic and olefinic contents on silica gel using the fluorescent indicator adsorption method (ASTM D1319-70), and the following fractions were collected:

- (i) saturated hydrocarbons
- (ii) mixture of saturated and olefinic hydrocarbons
- (iii) olefinic hydrocarbons
- (iv) mixture of olefinic and aromatic hydrocarbons
- (v) aromatic hydrocarbons
- (vi) mixture of aromatic hydrocarbons and polar compounds

The light oil product (LOP) boiling above 200°C and the deasphalted heavy oil product (maltenes of HOP) were separated into compound-type concentrates of saturates, monoaromatics, diaromatics, polyaromatics and basic compounds in a dual-packed (silica gel and alumina gel) liquid-solid chromatographic column developed by the API project 60 (4), and modified in this laboratory (5), Figure 1.

The number of moles of the various types of structures were determined using average molecular weights that were obtained by vapour-pressure osmometry for the light and heavy oil fractions. The average molecular weights of the light oil fraction below 200°C were determined from gas chromatographic simulated distillation data, assuming that the material distilling when half of the sample had distilled represented the average molecular weight. The aromatics in the light ends distilling below 200°C were assumed to be mononuclear aromatics.

The number of sulphur-bearing structures in each fraction was determined assuming that there was one sulphur atom per molecule; the number of sulphur-free structures was then obtained by difference. Sulphur contents of compound-types were determined by the microbomb method (6).

Characterization of the Hydrocracked Products

1. Capillary Gas Chromatography

The various fractions collected from the FIA separations were subjected to capillary gas chromatography on a 100 ft OV-101 column, and the column effluent was characterized by mass spectrometry (CEC-21-104).

2. Gas-liquid Chromatography (Packed Columns)

The main fractions of the hydrocarbon types collected from the liquid-solid chromatographic separation (LOP above 200°C and deasphalted HOP) were chromatographed on an OV-1 packed column using both flame ionization and coulometric sulphur detectors.

3. Separation on Anion-Cation Exchange Resins

The heavy oil product of a severely hydrocracked bitumen was subjected to chromatography on both anion and cation exchange resins in order to concentrate the nitrogenous and polar compounds according to a procedure similar to that developed by the API project 60 (7), but modified to reduce the time of analysis (8). The results were compared with results obtained on applying this separation scheme to the bitumen feedstock.

4. Infra-red Spectrometry

Some comparisons were made of the IR spectra on a Beckman IR-12. Methylene chloride solutions of the samples were scanned for the carbazole and carboxylic acid bands.

5. High Resolution Mass Spectrometry

The diaromatics of the hydrocracking product (445°C, LHSV 1) were studied by high resolution mass spectrometer (Model MS-9) for identification of individual components.

RESULTS AND DISCUSSION

Gross Composition

In thermal hydrocracking of Athabasca bitumen the lighter materials are formed at the expense of the heavier ones as shown in Table 1. The pitch fraction is defined as that fraction boiling above 523.9°C as determined in a Podbielniak flash equilibrium still (2). The extent of conversion is determined by the percentage of pitch converted to products distilling below 523.9°C.

Compound-Type Changes

In Table 2 the changes that occur in the chemical type distribution on a weight basis are shown. The saturated hydrocarbons (including the olefins) increased at the expense of the other classes of compounds, particularly the polynuclear aromatic and polar compounds and most of this increase (46%) took place at the least severe treatment (435°C) studied. The basic compounds decreased to less than half the amount in the feed during the mildest treatment but, since this class constitutes such a small proportion of the total bitumen, it does not make a substantial contribution to other compound types on degradation. The asphaltenes were not appreciably affected by the treatments at 435°C. The mononuclear aromatic compounds increased somewhat, while the dinuclear aromatic compounds decreased slightly.

Under the more severe conditions, the production of saturated hydrocarbons appears to accelerate as a function of the percentage of pitch conversion as shown in Figure 1. The asphaltenes diminish markedly when subjected to the more severe thermal treatments. The polynuclear aromatic and polar compounds continue to decrease on a weight basis with increasing severity of treatment, while the dinuclear aromatics undergo a small decrease and the mononuclear aromatic compounds increase slightly.

On a molar basis the situation is different, as shown in Table 3. The number of moles per 100 gm of products of all aromatic hydrocarbons increases as a function of severity of hydrocracking. Some of this increase is due to cleavage of lower molecular weight aromatic hydrocarbons from the higher molecular weight complex materials. The other possibility is that they could have been formed during aromatization reactions in which some structures, such as asphaltenes or large polynuclear aromatic clusters, become hydrogenated by hydrogen transfer.

The number of moles of both dinuclear and polynuclear aromatic hydrocarbons increase substantially during the less severe treatments, and during the most severe treatment the increase is not as substantial as in the lower conversion rates. The moles of mononuclear aromatic hydrocarbons increase steadily with the increase in severity of conditions.

When the changes in the number of moles of the various types are plotted against the percentage pitch conversion, the plots as shown in Figure 2 are obtained. The interesting feature of this figure is that the largest increases in the number of moles of mononuclear aromatic hydrocarbons, and also in the weight of saturated hydrocarbons, occur during the most rapid decline of the asphaltenes.

Asphaltenes are considered to consist mainly of large substituted aromatic structures (8) and to contain more heteroatoms than other bitumen fractions. Therefore it would be expected that their cleavage during cracking would increase the number of polynuclear aromatic and polar structures. While there is a steady molar increase in these compounds, there is no apparent direct relationship between their increase and the rate of asphaltene degradation.

The substantial increase in the number of moles of mononuclear aromatic compounds tends to indicate some relationship to asphaltene destruction. Since it is not believed that the asphaltenes contain many phenyl groups, a hydrogenation step of the large aromatic structures in the asphaltenes before undergoing cracking must be considered.

Mononuclear aromatic hydrocarbons are possibly formed during hydrogen transfer reactions in which asphaltenes undergo some hydrogenation, while cycloalkanes are aromatized. Cyclohexanes are not good hydrogen donors but decalins are (9). If a dicyclic alkane is a good donor, then more highly cyclic alkanes should be even better donors. If olefinic bonds are involved in the ring systems their tendency for aromatization is increased (10). It is known that the Athabasca saturated hydrocarbons are highly cyclic (11) and that the hydrocracked saturates contain substantial olefins. Thus mono-aromatization of the saturated hydrocarbons (including olefins) appears plausible.

The asphaltene aromatic clusters might also have undergone some hydrogenation during milder treatments in which cycloalkyl mononuclear (tetralins) or other cycloalkyl aromatic compounds lost hydrogen that led to the increase in di- and polynuclear aromatic moles. This would then suggest that the number of moles of mononuclear aromatic hydrocarbons produced is greater than indicated in Table 3.

The FIA results of the light ends below 200°C were as shown below:

		<u>Saturates</u>	<u>Olefins</u>	<u>Aromatics & Polar</u>
LHSV - 1,	400°C	60.6	26.8	12.7
	435	59.2	29.3	11.5
	445	69.7	19.2	11.1
	455	69.6	18.9	11.5
LHSV - 2,	445	73.0	15.9	11.1
	460	75.3	13.8	10.8

It can be seen that the olefin content of the light ends decreases with severity of cracking which may be caused by the aromatization reactions discussed earlier.

These light ends were virtually non-existent in the bitumen feedstock and thus were totally the products of hydrocracking. In Figure 3, the chromatogram of light ends obtained under mild conditions (400°C, LHSV-1, pitch conversion 27.69) is shown. Most of the main peaks (30% of the LOP) are due to normal alkanes. This proportion of normal alkanes appeared to increase slightly with an increase in hydrocracking severity.

Figure 4 shows the gas chromatogram of the aromatic compounds and the numbered peaks represent the following compounds.

1. n-propyl benzene
2. 1-methyl-4-ethyl benzene
3. 1,3,5-trimethyl benzene
4. 1,2,4-trimethyl benzene
5. } mixture of a methyl- isopropyl benzene and
6. } a trimethyl thiophene
7. a dimethyl-ethyl benzene
8. a dimethyl-ethyl benzene and dimethyl-ethyl thiophene
9. mixture of tetra-methyl benzene and tetramethyl thiophene
10. dimethyl indane and tetramethyl benzene

The chromatogram of the polar materials is shown in Figure 5. These materials are composed mostly of thiophenes but they also contain benzene and xylene isomers. The numbered peaks were identified as follows:

1. thiophene and benzene
2. ethyl thiophene
3. tetrahydrothiophene
4. p-xylene
5. m-xylene
6. o-xylene
7. 2-n-propyl thiophene
8. 2,3,4 - trimethyl thiophene

The amount of sulphur in the light ends increases up to a level of approximately 0.005 moles per 100 g of bitumen products and thereafter remains virtually constant with increasing hydrocracking severity, indicating a steady state between the sulphur-containing molecules cleaved from the high molecular weight components and those desulphurized to H_2S .

Dinuclear Aromatic Compounds

This class of compounds has been investigated to a considerable extent, especially with high resolution mass spectrometry. As far as the material that vaporized in the spectrometer was concerned (average carbon numbers for the naphthalenes were about 17.5 in the feed and about 16 in the severely cracked products),

there was little difference between the naphthalenes in the feed and products according to the mass spectra analyses. These naphthalenes were substituted by both alkyl and cycloalkyl groups with the latter predominating.

However, according to the gas chromatograms (FID), there are considerable differences between the dinuclear aromatic compounds in the feedstock and the hydrocracked products. As the products become more severely hydrocracked the molecular weight and the number of isomers decrease. This is shown in Figures 6-10. The compounds in the main diaromatic fraction of the feedstock are unresolvable by gas chromatography. In the severely hydrocracked products even the heavy oil, the main diaromatic fraction, is resolvable.

In the feedstock, alkyl and cyclo-alkyl benzothiophenes represent the sulphur compounds eluting from the liquid chromatographic column before and during the main diaromatic fraction elution. Alkyl and cyclo-alkyl dibenzothiophenes were predominant in the eluting tail of the diaromatic fraction. In the severely hydrocracked diaromatic fractions, the benzothiophenes were predominant in all fractions and small amounts of dibenzothiophenes were found only in the tail fractions. The sulphur compounds decrease in molecular weight and become more resolvable by gas chromatography with increasing hydrocracking as shown by the chromatograms in Figures 11-15.

Another aspect of the diaromatic compounds is the appearance of dibenzofurans in the tail fractions of the severely hydrocracked materials. These were not found in the feedstock and thus appear to be formed during hydrocracking.

As far as the polynuclear and polar fractions are concerned, they also become more resolvable on gas chromatography with increasing hydrocracking severity.

Other Changes During Hydrocracking

1. Decarboxylation

In Figure 16 we see the infra-red spectra in region $1650-1750\text{ cm}^{-1}$ of two acid fractions isolated from the bitumen. The fractions consisted of 2.7% and 0.8% of the bitumen. The infra-red spectra of the former is similar to alkyl acids and the latter to aromatic acids. In the hydrocracked material these acid fractions were virtually absent, as shown in Table 4, indicating complete decarboxylation.

2. Carbazole Formation

Comparisons are made in Figure 17 of the IR spectra of various fractions obtained by chromatography on ion exchange resins of the feed, and of a severely hydrocracked heavy oil. The results of the chromatography are shown in Table 4. The absorption band at 3460 cm^{-1} is considered to be due to carbazole (7). It can be seen that there is considerable increase in carbazoles during hydrocracking.

Sulphur Compounds in the Polynuclear and Polar Compound Classes

The amounts of sulphur compounds on a molar basis are shown in Table 5, in which it is assumed as a first approximation that each mole contains one sulphur atom. The fact that about two-thirds of the sulphur was lost in these fractions on hydrocracking indicates that a large portion of this class contains sulphur that is less thermally stable (possibly sulphides). Remaining sulphur compounds are considered to be mostly thiophenic.

TABLE 1

GROSS COMPOSITION OF ATHABASCA BITUMEN AND
PRODUCTS OF HYDROCRACKING
(wt % of total bitumen)

SAMPLE	PITCH CONVERSION*	GAS*	LIGHT OIL PRODUCT (LOP)		HEAVY OIL PRODUCT (HOP)	
			Below 200°C	Above 200°C	MALTENES	ASPHALTENES
FEED			1.4	(83.3% maltenes above 200°C)		15.3
LHSV-2, 435°C	59.1	3.9	7.0	10.2	65.5	13.4
LHSV-2, 445°C	68.9	4.0	11.5	10.2	62.0	12.3
LHSV-2, 455°C	77.4	5.9	13.1	10.8	59.7	10.5
LHSV-1, 445°C	80.0	6.8	13.5	25.7	47.0	7.0
LHSV-1, 460°C	91.4	9.2	18.5	34.0	35.6	2.7

(*) Reference 1

TABLE 2

COMPOUND TYPE DISTRIBUTION (% BY WT)

SAMPLE	SATURATES	MONONUCLEAR	DINUCLEAR	POLYNUCLEAR	POLAR	BASIC	ASPHALTENES
		AROMATICS	AROMATICS	AROMATICS	COMPOUNDS	COMPOUNDS	
FEED	21.0	7.8	11.0	20.1	19.0	5.7	15.3
LHSV-2, 435°C	33.4	9.3	10.5	14.2	12.8	2.3	13.4
LHSV-2, 445°C	36.1	10.1	10.7	12.9	11.6	2.1	12.3
LHSV-2, 455°C	38.9	10.5	11.0	11.7	9.8	1.6	10.5
LHSV-1, 445°C	42.5	10.5	10.1	11.1	10.5	1.2	7.0
LHSV-1, 460°C	47.8	11.5	9.7	9.1	8.8	0.9	2.1

TABLE 3

COMPOUND TYPE DISTRIBUTION
WITHOUT SULFUR COMPOUNDS (MOLES/100 g)

SAMPLE	MONONUCLEAR	DINUCLEAR	POLYNUCLEAR	POLAR COMPOUNDS
	AROMATICS	AROMATICS	AROMATICS	
FEED	0.017	0.012	0.004	-
LHSV-2, 435°C	0.026	0.021	0.011	0.005
LHSV-2, 445°C	0.030	0.023	0.014	0.00
LHSV-2, 455°C	0.036	0.028	0.015	0.010
LHSV-1, 445°C	0.039	0.027	0.021	0.014
LHSV-1, 460°C	0.046	0.030	0.020	0.016

TABLE 4

SEPARATION OF NITROGENOUS COMPONENTS
ON ANION-CATION EXCHANGE RESINS

<u>ELUENT</u>	<u>DEASPHALTED FEED</u> (MALTENES)		<u>DEASPHALTED HOP</u> (MALTENES)	
	<u>wt % Eluate</u>	<u>% N</u>	<u>wt % Eluate</u>	<u>% N</u>
n-Pentane	73.0	0.02	82.7	0.02
Cyclohexane	5.4	0.46	2.4	0.70
<u>Anion Exchange Resin A-29</u>				
Benzene	7.8	1.26	7.2	5.29
Benzene-Methanol	2.4	1.28	1.2	5.57
Benzene-Methanol-CO ₂	2.7	0.34	0.2	--
Benzene-Acetic Acid ²	0.8	2.95	0.1	--
<u>Cation Exchange Resin A-15</u>				
Benzene	4.5	0.64	2.0	2.07
Benzene-Methanol	1.8	0.92	0.4	--
Benzene-Methanol-Isopropylamine	1.6	2.14	1.9	7.32

TABLE 5

SULPHUR CONTENT DISTRIBUTION
(MOLES/100 g)

<u>SAMPLE</u>	<u>MONONUCLEAR</u> <u>AROMATICS</u>	<u>DINUCLEAR</u> <u>AROMATICS</u>	<u>POLYNUCLEAR</u> <u>AROMATICS</u>	<u>POLAR COMPOUNDS</u>
FEED	0.005	0.016	0.043	0.040
LHSV-2, 435°C	0.010	0.015	0.030	0.025
LHSV-2, 445°C	0.011	0.015	0.026	0.022
LHSV-2, 455°C	0.010	0.015	0.024	0.018
LHSV-1, 445°C	0.080	0.013	0.014	0.018
LHSV-1, 460°C	0.080	0.013	0.015	0.013

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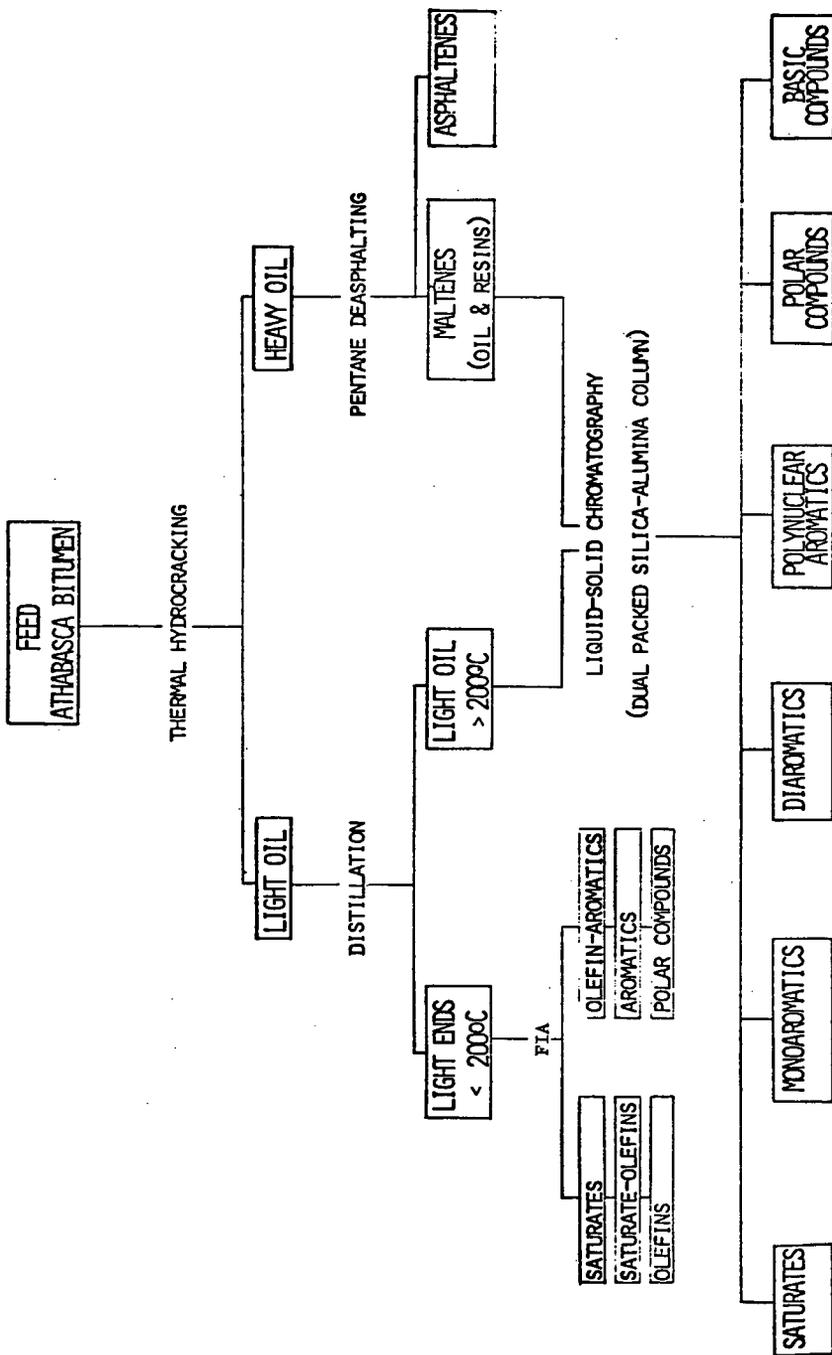
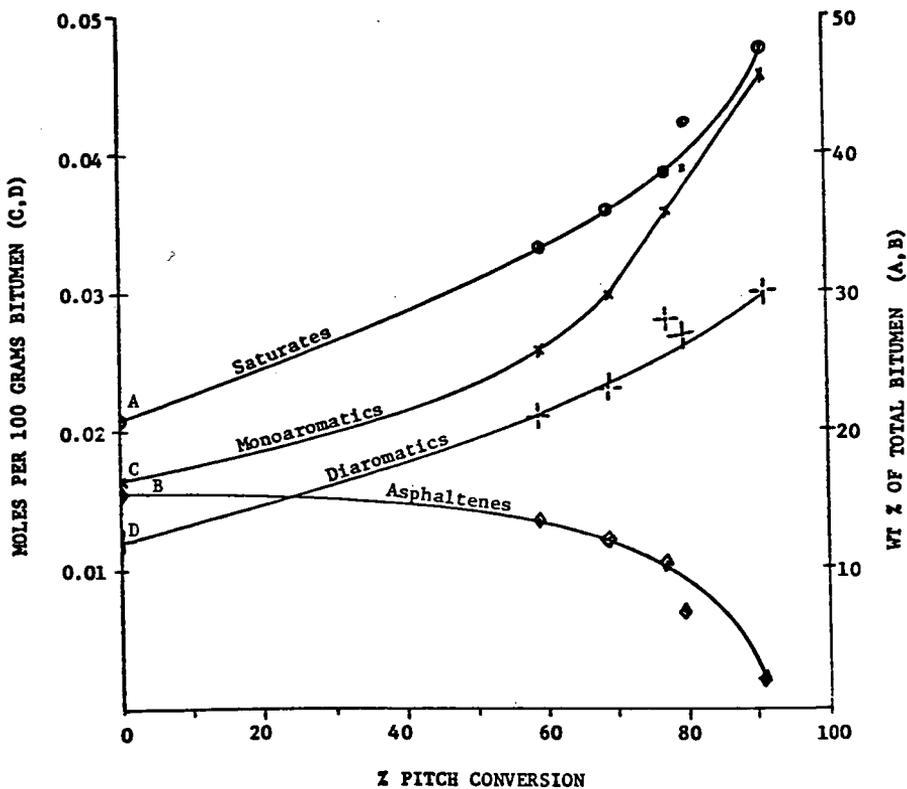


FIGURE 1 - HYDROCRACKING AND SEPARATION SCHEMATIC



The Effect of Hydrocracking on Saturate, Monoaromatic and Asphaltene Contents in Athabasca Bitumen

FIGURE 2

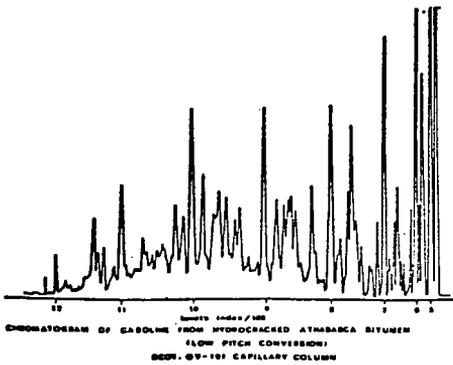


FIGURE 3

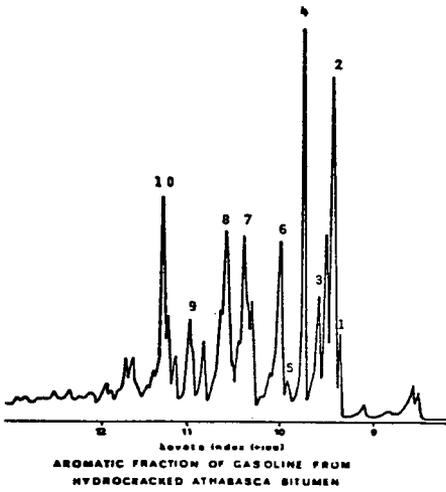


FIGURE 4

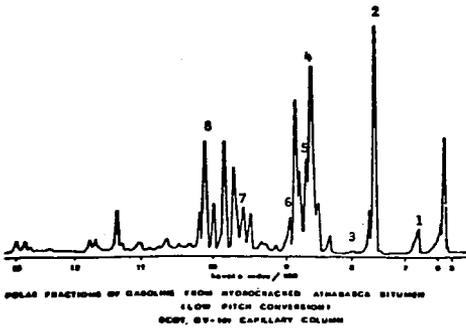


FIGURE 5

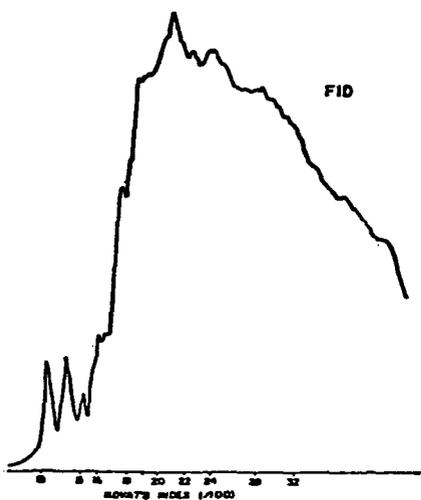


FIGURE 6
DIAROMATICS OF ATHABASCA FEEDSTOCK
Light Oil Product (above 200°C)
OV-1 on Chromosorb W, a.w., 60-80 m

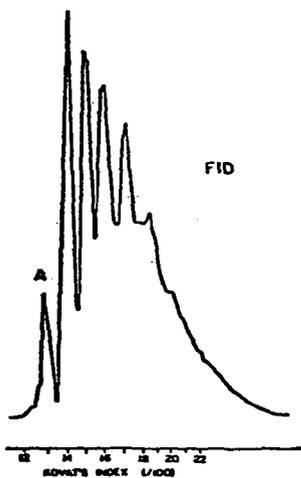


FIGURE 7
DIAROMATICS OF HYDROCRACKED ATHABASCA
(435°C, LHSV-2)
Light Oil Product (above 200°C)
OV-1 on Chromosorb W, a.w., 60-80 m

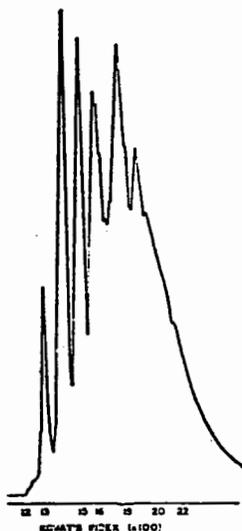


FIGURE 8

DIATOMICS OF HYDROCRACKED ATHABASCA
 (460°C, LHSV-1)
 Light Oil Product (above 200°C)
 OV-1 on Chromosorb W, a.w., 60-80 m

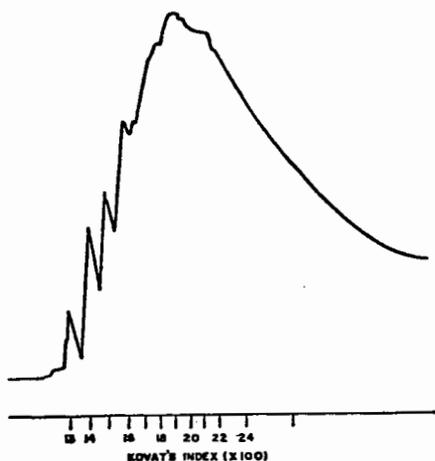


FIGURE 9

DIATOMICS OF HYDROCRACKED ATHABASCA
 (435°C, LHSV-2)
 Heavy Oil Product (deasphalted)
 OV-1 on Chromosorb W, a.w., 60-80 m

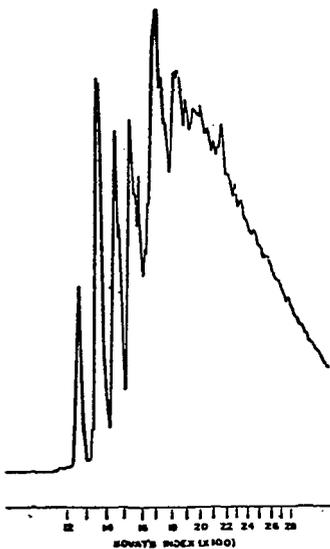


FIGURE 10

DIAROMATICS OF HYDROCRACKED ATHABASCA
 (460°C, LESV-1)
 Heavy Oil Product (deasphalted)
 OV-1 on Chromosorb W, a.w., 60-80 m

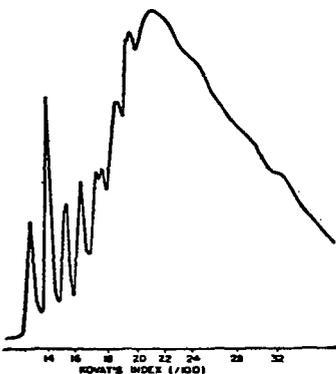


FIGURE 11

DIAROMATIC SULPHUR OF ATHABASCA FEEDSTOCK
 Light Oil Product (above 200°C)
 OV-1 on Chromosorb W, a.w., 60-80 m

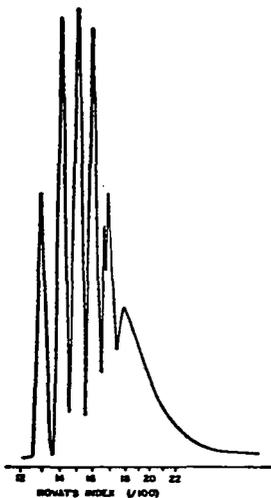


FIGURE 12

DIAROMATIC SULPHUR OF HYDROCRACKED
 ATHABASCA (435°C, LHSV-2)
 Light Oil Product (above 200°C)
 OV-1 on Chromosorb W, a.w., 60-80 m

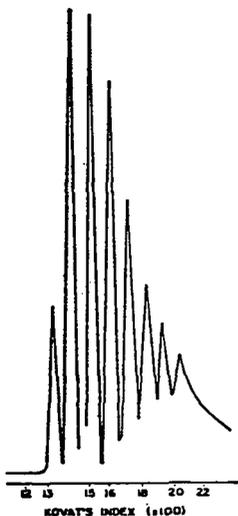


FIGURE 13

DIAROMATIC SULPHUR OF HYDROCRACKED
 ATHABASCA (460°C, LHSV-1)
 Light Oil Product (above 200°C)
 OV-1 on Chromosorb W, a.w., 60-80 m

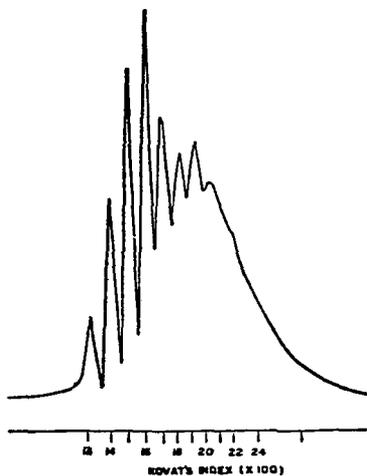


FIGURE 14
DIAROMATIC SULPHUR OF HYDROCRACKED
ATHABASCA (435°C, LHSV-2)
Heavy Oil Product (deasphalted)
OV-1 on Chromosorb W, a.w., 60-80 m

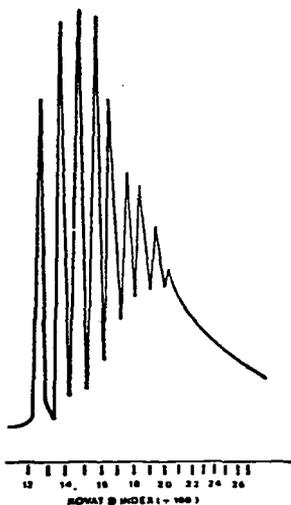


FIGURE 15
DIAROMATIC SULPHUR OF HYDROCRACKED
ATHABASCA (460°C, LHSV-1)
Heavy Oil Product (deasphalted)
OV-1 on Chromosorb W, a.w., 60-80 m

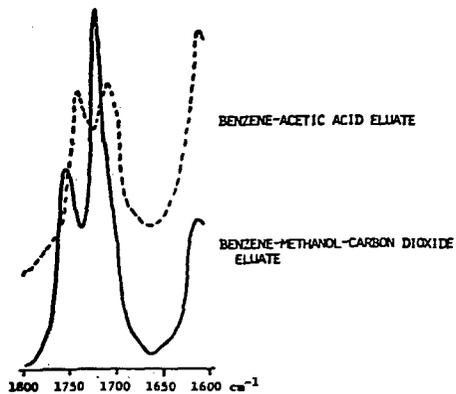


FIGURE 16

INFRA-RED SPECTRA OF ATHASASCA BITUMEN ACIDS.

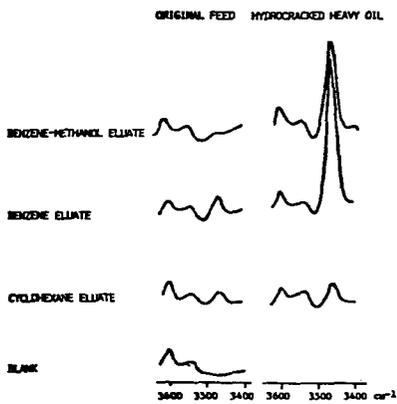


FIGURE 17

ATHASASCA BITUMEN; INFRA-RED SPECTRA OF ELLIATE FROM ANION EXCHANGE RESIN