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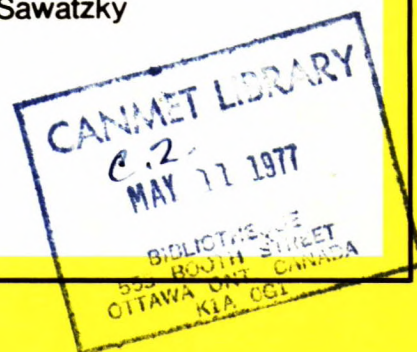
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# EFFECT OF THERMAL HYDROCRACKING ON THE DISTRIBUTION OF COMPOUND-TYPES IN ATHABASCA BITUMEN

A.E. George, R.C. Banerjee, G.T. Smiley and H. Sawatzky

Canadian Fossil Fuel Research Laboratory  
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EFFECT OF THERMAL HYDROCRACKING ON THE  
DISTRIBUTION OF COMPOUND-TYPES IN ATHABASCA BITUMEN

by

A.E. George<sup>\*</sup>, R.C. Banerjee<sup>\*\*</sup>, G.T. Smiley<sup>\*\*\*</sup> and H. Sawatzky<sup>\*</sup>

ABSTRACT

The changes in the chemical composition of Athabasca bitumen due to thermal hydrocracking under varying severities of treatment were studied. The main reaction appeared to be the cleavage of saturated hydrocarbon structures from aromatic clusters resulting in large increases in the saturated hydrocarbon fraction as well as decreases in molecular weights. The mononuclear aromatic fraction increased very substantially in weight with severity of treatment but the increase in the number of mononuclear aromatic structures was even more marked. The dinuclear aromatic fraction decreased in weight but the number of these structures increased. The polynuclear aromatic and polar fractions decreased markedly in weight but the number of polynuclear aromatic structures changed only slightly. The most severe treatment almost eliminated the asphaltenes and the basic materials. The changes in the sulphur contents of the various fractions were followed and are discussed. Attempts are made to partially explain the conversions during these treatments by thermal hydrogen transfer-aromatization reactions.

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L'EFFET DE L'HYDROCRAQUAGE THERMIQUE SUR LA DISTRIBUTION  
DE COMPOSES-TYPES DANS LE BITUME DE L'ATHABASCA

par

A.E. George\*, R.C. Banerjee\*\*, G.T. Smiley\*\*\* et H. Sawatzky\*

RESUME

Ce rapport présente une étude des changements produits dans la composition chimique du bitume de l'Athabasca par l'hydrocraquage thermique dans différentes conditions de traitement. Le plus important d'entre eux semble être le clivage de structures d'hydrocarbure saturé à partir d'amas de particules aromatiques; ce clivage provoqua un plus grand fractionnement d'hydrocarbure saturé en même temps que de plus petits poids moléculaires. Ainsi, la fraction mononucléaire aromatique devint beaucoup plus pesante lors d'un traitement sévère, tandis que le nombre de leurs structures augmenta encore plus. Le poids de la fraction dinucléaire aromatique diminua; par contre, le nombre de ses structures augmenta. Les fractions polaires et polynucléaires aromatiques, elles, diminuèrent considérablement de poids, et le nombre des structures polynucléaires aromatiques varia quelque peu. Le traitement le plus sévère élimina presque entièrement les asphaltènes et les matériaux basiques. On remarqua, de plus, des changements dans les contenus de soufre des différentes fractions; ceux-ci sont discutés. Et on essaya d'expliquer les convertissements pendant les transferts d'hydrogène thermiques - réactions d'aromatisation.

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## INTRODUCTION

The upgrading of Athabasca bitumen requires the use of pyrolytic processes. Coking processes are wasteful and hence alternate processes are being sought by the Department of Energy, Mines and Resources. One of the alternatives is thermal hydrocracking (1), and this report deals with the hydrocarbon-type conversions involved in hydrocracking asphaltic sulphurous bitumen under various conditions.

This work is carried out as part of the "Characteristics of Bitumen, Heavy Oils and Refined Products" project. Investigation of the hydrocracked bitumen products was made with the purpose of assessing their economic value, as well as obtaining a better understanding of the chemical reactions involved. This will lead to improved process-development and more productive refining operations.

Five samples of hydrocracked bitumen, selected to represent increasing severities of treatment as expressed in pitch conversion to distillable fractions, were subjected to analysis by liquid-solid chromatography. The experimental processes involved and the results are discussed in the following sections of this report.

## EXPERIMENTAL PROCEDURES

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

### Thermal Hydrocracking

The hydrocracking pilot plant and its operation have been described in a previous report (1). The reactor is a vertical vessel into which the 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, 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 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/h 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 (2).

### Distillation

The light oil was separated by distillation (ASTM D216-54) to light ends boiling below 200°C and a fraction boiling above 200°C. The heavy oil

did not contain any light ends boiling below 200°C. The distillation residue above 524°C under atmospheric pressure is defined as pitch.

#### Deasphalting

The asphaltene portion of the heavy oil 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 analyzed for saturate, aromatic and olefinic contents on silica gel using the fluorescent indicator adsorption method (ASTM D1319-70).

The light oil fraction boiling above 200°C and the deasphalted heavy oil (maltenes) were separated into compound-type concentrates of saturates, monoaromatics, diaromatics, polyaromatics, polar materials and basic compounds in a dual-packed (silica gel and alumina gel) liquid-solid chromatographic column developed by the API project 60 (3), and modified in this laboratory (4). In the modified procedure, the sample size was scaled down by a factor of 10 and pressure was applied to increase the speed of separation. The polyaromatics were eluted by benzene; the polar material was eluted by a mixture of polar solvents (methyl alcohol, ethyl ether and benzene) and the basic compounds were eluted by pyridine at 100°C (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. 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 the compound types were determined by the bomb method (5).

#### Mass Spectrometric Analyses

Analyses of the approximate compositions of the cyclic saturates were performed on a C.E.C. 21-104 mass spectrometer, operated at an ionization potential of 70eV and using electric scan.

### RESULTS

The Athabasca bitumen is a heavy, sulphurous oil with high asphaltene and metal contents. The chemical nature of its hydrocarbons is mostly aromatic (75% by weight) with a prevalent polyaromatic-polar composition of 70% of the aromatics. The properties of the bitumen are given in Table 1.

#### Effect of Thermal Hydrocracking on the Gross Composition

Increasing hydrocracking severity causes an increase in the amounts of light oil (Table 2) at the expense of the heavy oil and asphaltene contents. The asphaltene content diminishes from 15.3% in the feedstock and 13.4% at 435°C (LHSV-2) to 2.7% at 460°C (LHSV-1). This is an appreciable decrease, considering that the molecular weights of the treated asphaltenes also decline. Asphaltenes could be formed as well as destroyed in cracking reactions. The presence of hydrogen suppresses asphaltene formation in this reaction.

The severity of hydrocracking is more pronounced at the lower liquid hourly space velocity due to the increased residence time of the liquids in the reactor. A comparison of the pitch conversions of the two experiments at 445°C and space velocities of 1 and 2 is given in Table 2.

#### Effect of Thermal Hydrocracking on the Compound-Type Distribution

The compound-type distribution on a weight basis is shown in Table 3. The sulphur is included with the aromatic and polar types. Tables 4 and 5 show the number of moles per 100g of bitumen for the hydrocarbons and for the sulphur compounds respectively. Tables 6 and 7 show the total sulphur contents and molecular weights of the various compound-types.



### Saturated Hydrocarbons:

The total percentage of saturates in the liquid products of the bitumen increases markedly with increasing severity of hydrocracking, particularly in the light ends. Although the saturate content remains almost constant in the light oil fraction above 200°C, the increasing percentage of this fraction in the total product increases the total saturate content.

An approximate mass spectrometric ring-analysis of the saturates of the Athabasca bitumen shows that they are mainly cyclic with little or no alicyclics. About 90% of the cyclic material is dicyclic, tricyclic and tetracyclic in equal proportions. Monocyclics are absent, and pentacyclics or higher ring systems are present in only small amounts. The alicyclic hydrocarbons developed because of hydrocracking. The dicyclic and tricyclic systems prevailed, followed by the monocyclics, then the tetracyclics, or the reverse, depending on the boiling range investigated. Pentacyclic molecules decreased to trace amounts, while 6- and higher- ring structures disappeared.

The saturate content includes olefinic hydrocarbons ranging, in the light oil below 200°C, from 8.0% to 5.2% in the least and most severely hydrocracked products respectively. The range in the light oil products above 200°C is from 14.6% to 3.0%.

### Mononuclear Aromatics:

The monoaromatic content of the bitumen increases drastically (47%) at the highest pitch-conversion rate and 40% of this increase takes place at the mildest treatment (Table 3). The number of aromatic rings, however, increases 2.7 times (Table 4), mostly in the form of benzene structures in the light oil. Benzene compounds are valuable as chemical feedstocks and because of their combustion characteristics.

The numbers of sulphur structures in the monoaromatic concentrate, mostly thiophenes, double on the mildest treatment and then remain almost constant (Table 5).

### Dinuclear Aromatics:

This fraction's weight per cent decreases slightly on hydrocracking (Table 3) but the number of its diaromatic rings increases 2.5 times (Table 4). The thermal stability of the associated sulphur structures are indicated by their slight decrease (Table 5) with no evidence of formation from the destruction

of higher molecular-weight components. We have evidence (6) that most of these sulphur compounds are alkyl benzothiophenes.

#### Polynuclear Aromatics:

The weight per cent of this fraction decreases by more than 50% on hydrocracking, and 54% of this decrease occurs at the least severe treatment (Table 3). However, the number of the polyaromatic structures increases 2.75 times in the mildest treatment, then gradually to 5 times at 460°C (Table 4). The associated sulphur components are unstable relative to the diaromatic sulphur structures (Table 5) and they decrease by 30% with the mildest treatment. This percentage increases gradually to 65% at 460°C.

#### Polar Components:

Although this fraction diminishes in weight with hydrocracking similar to the polynuclear aromatics (Table 3), the number of polar structures increase (Table 4). The polar sulphur structures are thermally unstable and decrease by 68% at 460°C (Table 5).

#### Basic Compounds:

More than half of these compounds are destroyed at the mildest temperature, and only 15% remain at 460°C.

### DISCUSSION

The increase of the saturated hydrocarbons is caused by the cleavage of aliphatic components from the aromatic, polar and asphaltenic structures. At the mildest treatment this fraction appears to increase mostly at the expense of the polynuclear aromatics and the polar materials. The other types would also lose paraffinic and cyclic portions to the saturate fraction and in the meantime receive the same from the higher molecular weight complex fractions. The saturated hydrocarbons could, to a large extent, represent cleavage products from the asphaltenes, especially in the last two treatments. There is a strong relationship between the rate of asphaltene destruction and the increase in saturates content (Tables 1, 2 and Figure 2).

There is also a relationship between the mole increase of the sulphur-free monoaromatic structures (benzenes) and the degree of asphaltene

conversion (Figure 2) which suggests that these benzenes are cleaved from the complex asphaltenic structures. However, they could be generated by the aromatization of cycloalkanes.

Asphaltenes are considered to consist mainly of large substituted polynuclear aromatic structures (7) and to contain more heteroatoms than the other bitumen fractions. Therefore, it would be expected that their cleavage during cracking should increase the polynuclear aromatic structures as well as the polar compounds. While there is a steady increase in these fractions (Table 4), there is no direct relationship between this increase and the rate of asphaltene destruction.

The only compound-types that increase in sufficient quantity to explain the diminishing asphaltene content in the two most severe treatments are the saturates and the mononuclear aromatics. Since it is not plausible to assume that the asphaltenes consist largely of benzene structures, a hydrogenation step of the asphaltene clusters before undergoing cracking must be considered to explain the increase in monoaromatics.

It is unlikely that hydrogenation consumes appreciable molecular hydrogen and the major consumption is probably due to reaction with free radicals formed on cracking, unless some inorganic components in the bitumen catalyze hydrogenation. Probably the hydrogenation of most of the polynuclear aromatic clusters in the asphaltenes and some of the polynuclear aromatic fractions occur by hydrogen transfer reactions (8). Tetralins are good hydrogen donors in these reactions but, if this is the case, then there would be an appreciable increase in the dinuclear aromatic structures of the products where asphaltenes decrease sharply. This was not observed.

It is known that cyclohexanes are not good hydrogen donors but decalins are (7). If the addition of one aliphatic ring to cyclohexane would increase its hydrogen-donating capability greatly, then it can be inferred that the addition of more saturated rings would result in even better donors. The saturated hydrocarbons are highly cyclized and thus should be effective hydrogen donors. For these reasons, it can be argued that the large complex aromatic clusters become hydrogenated during the hydrocracking reactions by hydrogen resulting from aromatization of saturated structures and that the hydrogenated structures undergo more extensive cracking. This explains the large increase in both the benzene structures and saturated hydrocarbons.

## ACKNOWLEDGEMENT

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TABLE 1

PROPERTIES OF ATHABASCA BITUMEN

Specific Gravity, 60/60°F	1.009
Sulphur, wt%	4.63
Ash, wt%	0.68
Viscosity, cSt at 210°F	152.2
Conradson Carbon Residue, wt%	12.8
Asphaltene (pentane insolubles), wt%	15.3
Benzene Insolubles, wt%	0.9
Nickel, ppm	70.
Vanadium, ppm	190.

TABLE 2

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

<u>SAMPLE</u>	<u>PITCH CONVERSION*</u> <u>wt %</u>	<u>GAS*</u>	<u>LIGHT OIL</u>		<u>HEAVY OIL</u>	
			<u>Below 200°C</u>	<u>Above 200°C</u>	<u>MALTENES</u>	<u>ASPHALTENES</u>
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 3

COMPOUND TYPE DISTRIBUTION (% BY WT)

		<u>SATURATES</u>	<u>MONONUCLEAR AROMATICS</u>	<u>DINUCLEAR AROMATICS</u>	<u>POLYNUCLEAR AROMATICS</u>	<u>POLAR COMPOUNDS</u>	<u>BASIC COMPOUNDS</u>	<u>ASPHALTENES</u>
FFED		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	2.7

TABLE 4

COMPOUND TYPE DISTRIBUTIONWITHOUT SULPHUR COMPOUNDS (MOLES/100 g)

<u>SAMPLE</u>	<u>MONONUCLEAR AROMATICS</u>	<u>DINUCLEAR AROMATICS</u>	<u>POLYNUCLEAR AROMATICS</u>	<u>POLAR COMPOUNDS</u>
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	0.008
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 5

SULPHUR CONTENT DISTRIBUTION  
(MOLES/100 g)

<u>SAMPLE</u>	<u>MONONUCLEAR AROMATICS</u>	<u>DINUCLEAR AROMATICS</u>	<u>POLYNUCLEAR 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

TABLE 6

SULPHUR CONTENT OF COMPOUND-TYPES  
IN PRODUCTS OF HYDROCRACKING

	MONOAROMATICS		DIAROMATICS		POLYAROMATICS		POLAR MATERIAL	
	LO*	HO*	LO	HO	LO	HO	LO	HO
LHSV-2, 435°C	3.45	2.47	7.75	4.68	6.90	6.73	8.09	6.12
LHSV-2, 445°C	2.14	2.38	5.90	4.62	6.10	6.50	7.43	6.00
LHSV-2, 455°C	2.01	2.04	4.95	4.80	6.10	6.70	7.52	5.90
LHSV-1, 445°C	2.00	1.49	5.00	4.00	5.80	5.32	6.62	5.43
LHSV-1, 460°C	2.00	1.40	4.32	4.12	5.80	5.22	5.68	4.40

\* LO = light oil

\* HO = heavy oil

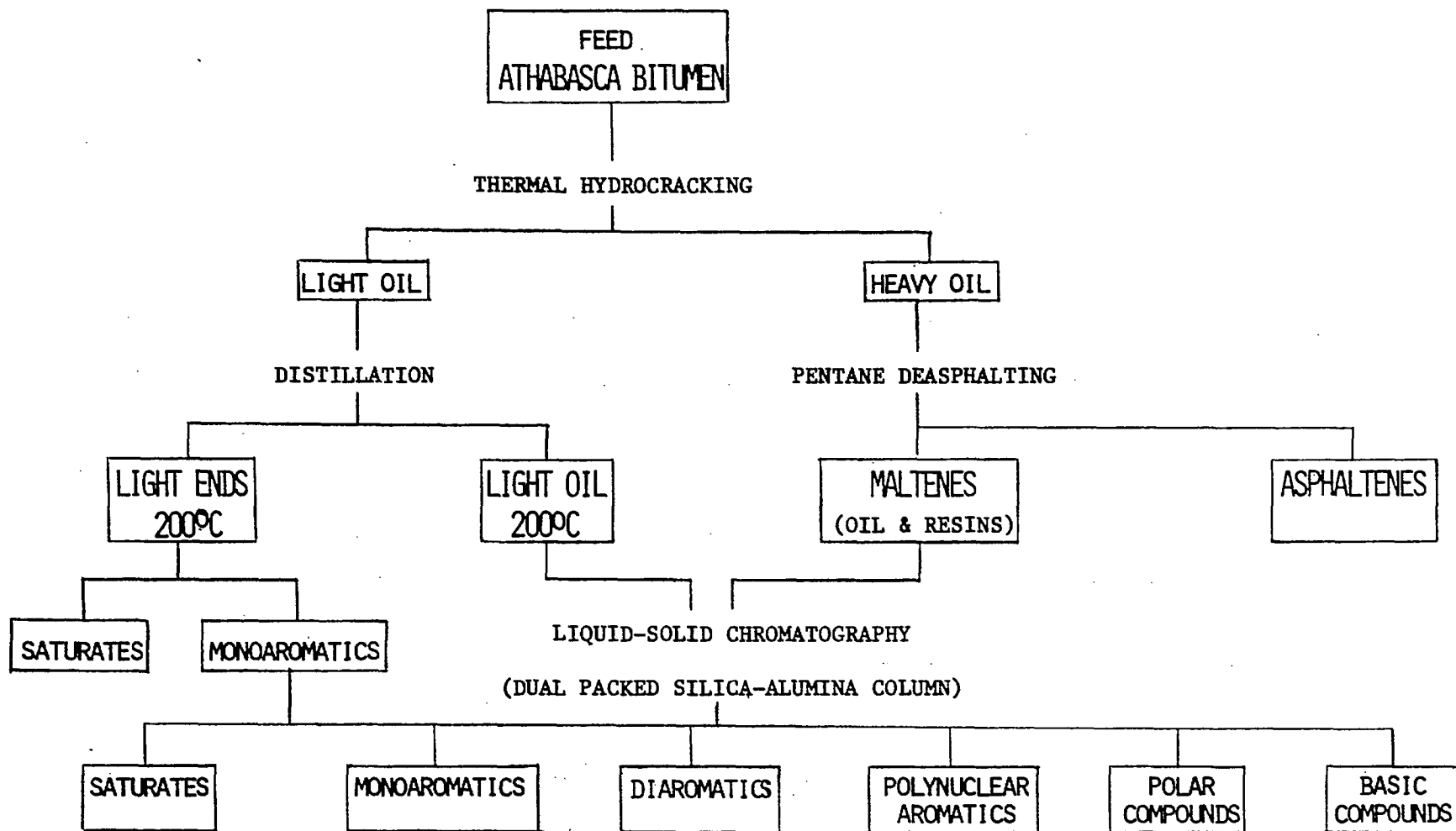
TABLE 7

MEAN MOLECULAR WEIGHTS OF THE  
COMPOUND TYPES IN PRODUCTS OF HYDROCRACKING

	MONOAROMATICS			DIAROMATICS		POLYAROMATICS		POLAR MATERIAL	
	LO* <200°C	LO >200°C	HO*	LO	HO	LO	HO	LO	HO
LHSV-2, 435°C	120	222	336	202	309	228	355	260	436
LHSV-2, 445°C	120	222	313	202	294	228	330	260	398
LHSV-2, 455°C	120	222	295	202	280	228	305	249	359
LHSV-1, 445°C	120	222	295	202	275	228	290	249	359
LHSV-1, 460°C	120	222	295	202	269	228	274	249	331

\* LO = light oil

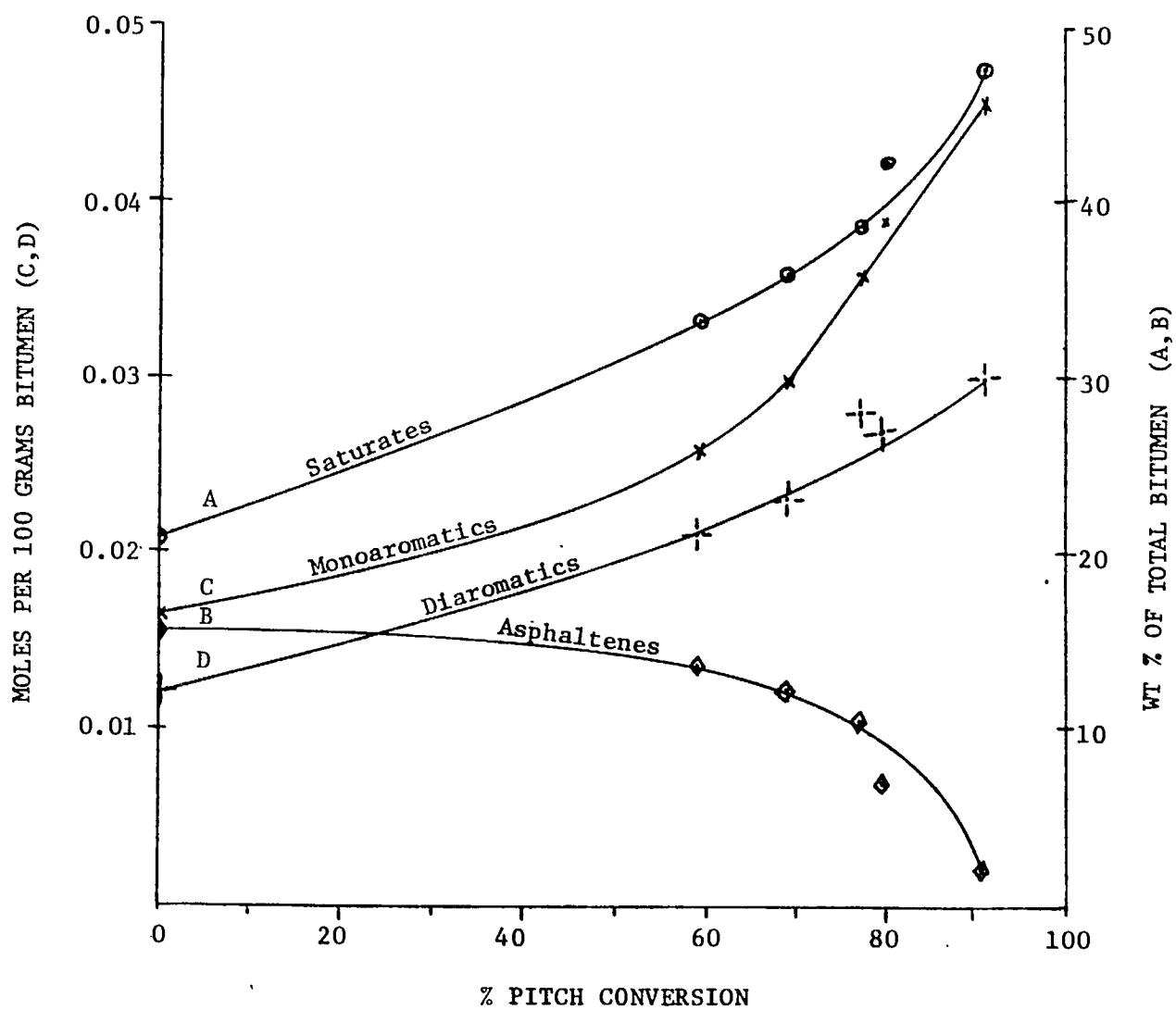
\* HO = heavy oil



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HYDROCRACKING AND SEPARATION (SCHEMATIC)

FIGURE I



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

FIGURE 2

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- 76-23 Catalysts for Hydrocracking and Refining Heavy Oils and Tars Part 2: The Effects of Molybdenum Concentration and of Zinc to Molybdenum Ratio on Desulphurization and Denitrogenation; R.J. Williams, M. Ternan and B.I. Parsons;  
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