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Centre canadien de la technologie des minéraux et de l'énergie

DEVELOPMENT OF A RAPID CHROMATOGRAPHIC PROCEDURE FOR THE IDENTIFICATION OF HYDROCARBON COMPONENTS IN THE NAPHTHA FRACTION OF HYDROCRACKED ATHABASCA BITUMEN

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INTRODUCTION

The upgrading of the heavy, sulphurous, asphaltic Canadian bitumens and oils is achieved through pyrolytic processes. Coking processes are wasteful and hence alternates, e.g. hydrocracking (1) are being sought by the Department of Energy, Mines and Resources. This report is an attempt to establish a rapid and reproducible method for the chemical characterization of the naphtha fraction of the hydrocracked product of these bitumens and oils. A catalytic hydrocracked product of Athabasca bitumen (see operating conditions in the Experimental Section) was selected as a typical synthetic fuel product for carrying out this study.

The need for a rapid method to determine the detailed hydrocarbon composition of full range naphtha in synthetic fuels has been evident since ERL started the hydrocracking pilot plant investigations. Quick-on-the-line characterization of products is needed to monitor the effect of altering processing conditions to meet certain product quality requirements.

EXPERIMENTAL

A schematic showing all the separation and identification steps described in this report, is shown in Figure 1.

Hydrocracking

The hydrocracking of Athabasca bitumen (Great Canadian Oil Sands sample described in Table I) was carried out using a one barrel per day pilot plant, the operating details of which have been described elsewhere (1). A coal-base catalyst, described in a previous CANMET report (2) was used at 460° C, 2000 psi and a space velocity of 2 h⁻¹ resulting in pitch conversion of 82.5% by weight. The catalyst consisted of 15% by weight of cobalt and molybdenum oxides and 85% coal.

Distillation

The light oil from the catalytic hydrocracking product was distilled (ASTM D216-54) to separate the naphtha fraction boiling up to 200^oC. This fraction was used to develop the chromatographic-mass spectrometric procedure.

Samples

The following samples were gas chromatographed:

- (1) 52 pure petroleum hydrocarbons, including straight-chain and branched alkanes, cycloparaffins, olefins and aromatics (Table II). All these compounds were diluted with n-pentane by a factor of 50 before chromatography.
- (2) Hydrocarbon-type concentrates of saturates, olefins and aromatics separated from the naphtha of the catalytic hydrocracking product of Athabasca bitumen by a modified Fluorescent Indicator Adsorption preparative column, described later in this report.
- (3) Total naphtha fraction (up to 200°C) from the catalytic (cobalt molybdenum/coal) hydrocracking product of Athabasca bitumen.

Total Sulphur Content

The INAX X-ray fluorescence spectrometer was used for sulphur content determination.

Hydrocarbon-Type Separation

A micro-scale preparative column was used to separate hydrocarbontype concentrates of saturates, olefins and aromatics from the hydrocracking naphtha. This column is a modification of the FIA method (ASTM D1319-70) using the same eluent (isopropanol), silica gel and fluorescent indicator, in a micro-scale glass column (Figure 3). The column tip was placed in a receiver manufactured in our laboratory. The receiver consisted of a 6 mm o.d. (3.5 mm i.d.) glass tube tapered, sealed and fitted into a 1 ml. vial filled with isopropanol. The vial was cooled in a dry ice container. With careful fitting, this configuration of receiver reduced losses of volatiles and eliminated freezing of the eluent in the column tip, experienced when the receiver was placed directly into the ice bath. The column was charged with 10 μ l of sample. The three bands seen under the ultraviolet light were collected in the order: saturates, olefins and aromatics in three separate vials. 1.2 μ l aliquots from each fraction were injected directly into the gas chromatograph.

Gas Chromatography

The instrument used was a Victoreen Model 4400 gas chromatograph with flame ionization detector, a Hewlett-Packard model 5100B 1 mV recorder and an Autolab model 6300 integrator. The injector on the gas chromatograph was replaced with an Open Tubular Column All-glass Injector System (Perkin-Elmer Corporation) with a split ratio of 200:1. A Support-Coated Open Tubular (SCOT) stainless steel capillary column (30 mm x 0.005 mm i.d.) was used for the chromatographic separations. The column coated with OV-101, was conditioned by passing helium gas at a flow rate of 4 ml per minute and programming the temperature at 2°C per minute starting at room temperature up to 175°C; holding at this temperature for 6 hours; programming up to 250°C at 1°C per minute; holding for 30 minutes turning the heater off and allowing the column to cool to 100°C. The column temperature was maintained at 100°C overnight. This column conditioning technique proved most successful in reducing column bleed, particularly in mass spectral analyses. The injection system was maintained at 210°C and the detector at 310°C. After the gas chromatograph reached an equilibrium temperature of 40°C, a 1.2 µl sample was injected. The column was held at 40°C for 5 minutes and then programmed at 2°C per minute to 170°C. Retention data from at least five reproducible chromatograms were used to calculate the Kovat's Index for each compound.

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Mass Spectral Data

Mass spectral analyses were performed using a Finnigan 4000 gas chromatograph-quadrupole mass spectrometer interfaced to an Incos Nova 1 computer. A SCOT capillary column coated with OV-101 and conditioned as above was used for the GC/MS analyses.

RESULTS AND DISCUSSION

Results on the compound-type distribution of the nitrogen and sulphur components in the hydrocracked naphtha of Athbasca bitumen have been reported by our laboratory (3,4). In this study the distribution of hydrocarbons of various types in the naphtha of Athabasca bitumen has been investigated.

Pure Petroleum Hydrocarbons

The retention data of the 52 pure petroleum hydrocarbons chromatographed in the system, and expressed as Kovat's Indices, are shown in Table II. These hydrocarbons range in boiling points from 36° C to 270° C which adequately covers the naphtha boiling range and allows for the incorporation of material boiling higher than 200° C in distillation. These hydrocarbons also represent a variety of hydrocarbons i.e. n-alkanes, isoalkanes, cycloalkanes, olefins and aromatics covering a range from C₅ to C₁₅. Figure 2 gives an indication of the linearity of elution of these hydrocarbons on the used SCOT column coated with OV-101, relative to their boiling points.

Naphtha from Catalytic Hydrocracking

Characteristics of the naphtha fraction employed in the hydrocarbontype separation as well as the gas chromatography-mass spectrometric (GC/MS) analysis are given in Table I. The chain and cyclic alkanes constitute 67.4% of the sample. The olefinic content is also relatively high, 22.1%, reflecting the cracking aspects of the process which the bitumen has undergone in the pilot plant.

(1) Hydrocarbon-type Separation:

The separation of the naphtha sample into saturated, olefinic and aromatic hydrocarbon fractions was undertaken to improve the resolution of components in the subsequent gas chromatographic analysis. The chromatograms of these hydrocarbon-type fractions separated by the micro-scale preparative FIA column, were considerably useful in establishing Kovat's Indices. Compounds could be identified which otherwise would coelute on the chromatographic column, when a total naphtha is used, making the identification of speculative nature. Comparison of the chromatographic data for the pure compounds with those of the hydrocarbon-type fractions provided correlations between retention characteristics and molecular structure. This information was particularly useful in the mass spectral interpretations.

(2) GC/MS of the Total Naphtha:

The total naphtha sample, without prior separation to hydrocarbon-type concentration was chromatographed on the SCOT column and individual peaks were identified by the quadrupole mass spectrometer using the data system. It was possible to identify 106 different hydrocarbon compounds (Table III) in the 80 resolved peaks from the naphtha chromatogram (Figure 4). This represents 97% by volume of the total naphtha fraction.

Chromatographing the entire naphtha sample under the established conditions had its definite advantages. When a sample is being supplied as a chromatographic peak directly to the mass spectrometer, a varying sample concentration can distort the spectrum (5). This effect came into play when we analyzed the hydrocarbon-type fractions, e.g. the olefin fraction showed severe peak tailing and considerable mass spectrum distortion. Coelution effects and associated component elution effects, i.e. compound that elutes near the compound of interest, considerably affect the mass spectral pattern obtained. By chromatographing the entire naphtha sample, peak elution was more symmetrical and mass spectral patterns more reproducible and thus easier to interpret.

ACKNOWLEDGEMENT

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TABLE I

Chemical Characteristics of the Hydrocracking Naphtha Fraction Used for GC/MS Analysis

Boiling range, ^O C	-200
Sulphur, wt %	0.32
Nitrogen, wt %	0.10
Saturates, vol %	67.4
Olefins, vol %	22.1
Aromatics, vol %	10.5

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Kovat's	Retention	Indices	for	Reference	Hydrocarbon	Compounds
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•	TABLE II		
	Kovat's Retention Indices for Reference Hydr	cocarbon Compounds	
	Compound	K.I.	
	n-Pentane	500	
	2.2 - dimethylbutane	536.8	
	2.3 - dimethylbutane	536.8	
•	2 - nentene	536 8	
	2 - pencene	573 7	
	2 - methylpentane	573.7	
	4 - methylpentene-2 (cis + trans)	5/3./	
	4 - methylpentene-1	584.2	
	3 - methylpentane	589.5	
	n-Hexane	600	
	2 - methylpentene-1	606.8	
	Hexene-1	606.8	
	2 - ethyl-butene-1	613.6	
	Hexene-2	627.2	
	Benzene	652.3	
	Cyclohexane	656.8	
	2.3 - dimethylpentane	665.9	
,	3 - methylbevane	675 0	
	2.2.4 trimethylnentene	699 6	
	2,2,4 - trimethyipentane	700	
	п-нертапе	700	
	Heptene-1	/11.3	
	Methylcyclohexane	/18.3	
	Heptene-3	719.7	
	Heptene-2 (cis + trans)	726.8	
	2,4 - dimethylhexane	733.8	
	2,5 - dimethylhexane	733.8	
	2,3,4 - trimethylpentane	749.3	
	Toluene	759.2	
	3 - methvlheptane	778.9	
	2.25 - trimethylbexane	788 7	
	n-Octane	800	
	Octope-1	813.8	
	ais = 1.2 = dimothyleyelehoropo	827 6	
	2 othulhemens 1	027.0	
	2 - ethymexene-i	032.2	
	Uctene-2	839.1	
	Ethylbenzene	854.0	
	m-xylene	863.2	
	p-xylene	863.2	
	o-xylene	886.2	
	n-Nonane	900	
	Cumene	915.9	
	Nouene-1	917.0	
•	p-cymene	951.1	
	Mesitylene	964 8	
	n-Decane	1000	
• .		1017 0	
	DECENE	1011.9	

TABLE II Cont'd

Compound K.I. n-Propylbenzene 1021.4 n-Butylbenzene 1051.2

1051.2
1100
1200
12`56.5
1300
1400
1467.2
1500

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TABLE III

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Hydrocarbon Components Identified in the Naphtha Fraction of the Hydrocracked Athabasca Bitumen (See Figure 3)

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Peak No.	Component	B.P. (^O C)
2butene-16.263butane-0.504pentene-129.975n-pentane36.076{cis - 2-pentene36.357cyclopentene44.2482,2 - dimethylbutane49.7494-methyl-pentene-153.88102-methyl-2-pentene67.7011n-hexane68.84trans - 2-hexene68.84trans - 2-hexene67.87131-methyl-1-cyclopentene70.4415methyl-lexane-2pentene80.1016benzene80.1017cyclohexane80.14183-methyl-hexane98.5020n-heptane98.5321heptene-298.5022methylcyclohexane100.9323ethylcyclohexane103.47242-methyl-3-ethylpentane113.47252,3,3 - trimethylpentane114.7627{2,3,3 - trimethylpentane113.4728{1-methyl-clos-3-ethylcyclopentane123.6230n-octane123.6231 $1,3 - dimethylcyclohexane123.6232octene-1120.00332,2,4-trimethylcyclohexane123.62342,3,5-trimethylcyclohexane123.62352,2,4-trimethylcyclohexane123.62367,4-dimethylcyclohexane123.6237\{1,3 - dimethylcyclohexane123.6231\{1,4 - dimethylcycloh$	1	isobutane	- 11 73
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	butene-1	- 6.26
4 pentene-1 29.97 5 n-pentane 36.07 6 $(cis - 2-pentene$ 36.35 7 cyclopentene 44.24 8 2, 2 - dimethylbutane 49.74 9 4-methyl-pentene-1 53.88 10 2-methyl-2-pentene 67.70 11 n-bexane 67.70 12 $(cis - 2-hexene$ 68.74 13 1-methyl-1-cyclopentene 72 14 3-methyl-1-cyclopentene 72 15 methyl-trans-2-pentene 70.44 16 benzene 80.10 17 cyclohexane 80.74 18 3-methyl-hexane 91.85 19 cis - 1,3 - dimethylcyclopentane 91.73 20 n-heptane 98.63 21 heptene-2 98.50 22 methylcyclohexane 100.63 23 ethylcyclohexane 10.63 24 2-methyl-s-sethylpentane 114.76 2,3,3 - trimethylpentane 114.76 2,3,4 - trimethylpentane 112.40	3	butane	- 0.50
5 n-pentane 36.07 6 {cis - 2-pentene 36.94 trans - 2-pentene 36.35 7 cyclopentene 44.24 8 2,2 - dimethylbutane 49.74 9 4-methyl-pentene-1 53.88 10 2-methyl-2-pentene 68.74 11 n-hexane 68.74 12 {cis - 2-hexene 68.84 trans - 2-hexene 70.70 13 1-methyl-1-cyclopentene 72 14 3-methyl-trans-2-pentene 70.44 15 methyl-ylcyclopentane 71.81 16 benzene 80.10 17 cyclohexane 98.50 18 3-methyl-hexane 91.85 19 cis - 1,3 - dimethylcyclopentane 91.85 19 cis - 1,3 - dimethylcyclopentane 100.93 21 heptene-2 98.50 22 methyl-scilopentane 103.47 24 2-methyl-3-ethylpentane 114.76 25 2,2,3 - trimethylpentane 114.76 2,3,4 - trimethylpentane <	4	pentene-1	29.97
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10Definition17cyclohexane 80.74 18 $3-methyl-hexane$ 91.85 19cis - 1,3 - dimethylcyclopentane 91.73 20n-heptane 98.43 21heptene-2 98.50 22methylcyclohexane 100.93 23ethylcyclohexane 103.47 242-methyl-3-ethylpentane 115.65 252,2,3 - trimethylpentane 106.33 26toluene 110.63 27 $\{2,3,3 - trimethylpentane$ 113.47 28 $\{1-methyl-cis-3-ethylcyclopentane$ 121.52 1-methyl-cis-3-ethylcyclopentane 121.40 291-trans-2-dimethylcyclohexane 122.67 31 $\{1,3 - dimethylcyclohexane$ 122.00 32octene-1 122.00 33 $2,2,4-trimethylhexane$ 131.34 351-cis-2-dimethylcyclohexane 122.00 36 $\{2-ethylhexene$ 120.00 37ethylbenzene 136.19 381.1.3-trimethylocyclohexane 126.65	16	bongono	80 10
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242-methylpertaile113.03252,2,3 - trimethylpentane109.8426toluene110.6327 $\{2,3,3 - trimethylpentane$ 114.7628 $\{2,3,3 - trimethylpentane$ 113.4728 $\{3-methylheptane$ 118.191-methyl-cis-3-ethylcyclopentane121.521-methyl-1-ethylcyclopentane123.4230n-octane125.6731 $\{1,3 - dimethylcyclohexane$ 126.5432octene-1122.00332,2,4-trimethylhexane131.34351-cis-2-dimethylcyclohexane129.7336 $\{2-ethylhexene$ 120.00octene-2125.637ethylhezane136.19381,1.3-trimethylcyclohexane136.19	25	2-methyl-3-ethylpentane	115 65
252,2,3 - trimethylpentale109.0426toluene110.6327 $\{2,3,3 - \text{trimethylpentane}$ 114.762,3,4 - trimethylpentane113.473-methylheptane118.191-methyl-cis-3-ethylcyclopentane121.521-methyl-1-ethylcyclopentane123.4230n-octane125.6731 $\{1,3 - \text{dimethylcyclohexane}$ 120.901,4 - dimethylcyclohexane118.3532octene-1122.00332,2,4-trimethylhexane131.34351-cis-2-dimethylcyclohexane131.3436 $\{2-\text{ethylhexene}$ 120.00octene-2125.637ethylbenzene136.19381.1.3-trimethylcyclohexane136.63	24 25 ↓	2 - methy = -3 - ethy = pentane	100 84
20110.0327 $\{2,3,3 - trimethylpentane$ 114.7628 $\{2,3,4 - trimethylpentane$ 113.473-methylheptane118.191-methyl-cis-3-ethylcyclopentane121.521-methyl-1-ethylcyclopentane123.4230n-octane125.6731 $\{1,3 - dimethylcyclohexane$ 120.901,4 - dimethylcyclohexane118.3532octene-1122.00332,2,4-trimethylhexane131.34351-cis-2-dimethylcyclohexane129.7336 $\{2-ethylhexene$ 120.0037ethylbenzene136.19381.1.3-trimethylcyclohexane136.63	26	tolueno	110 63
27 $73,3,5$ $114,76$ $2,3,4$ trimethylpentane $113,47$ 3 -methylheptane $118,19$ 1 -methyl-cis-3-ethylcyclopentane $121,52$ 1 -methyl-1-ethylcyclopentane $121,40$ 29 1-trans-2-dimethylcyclohexane $123,42$ 30 n-octane $125,67$ 31 $\begin{cases} 1,3 - dimethylcyclohexane120,901,4 - dimethylcyclohexane118,3532octene-1122,00332,2,4-trimethylhexane126,54342,3,5-trimethylhexane129,7336\begin{cases} 2-ethylhexene125,637ethylbenzene136,19381,1,3-trimethylcyclohexane136,63$	20	(2,3,3,- trimethylpentane	114 76
28 3 -methylheptane 118.19 28 1 -methyl-cis-3-ethylcyclopentane 121.52 1 -methyl-l-ethylcyclopentane 121.40 29 1 -trans-2-dimethylcyclohexane 123.42 30 n -octane 125.67 31 $\begin{cases} 1, 3 - \text{ dimethylcyclohexane} \\ 1, 4 - \text{ dimethylcyclohexane} \\ 1, 4 - \text{ dimethylcyclohexane} \\ 122.00$ 32 octene-1 122.00 33 $2, 2, 4$ -trimethylhexane 126.54 34 $2, 3, 5$ -trimethylhexane 131.34 35 1 -cis-2-dimethylcyclohexane 129.73 36 $\begin{cases} 2$ -ethylhexene octene-2 125.6 37 ethylbenzene 136.19 38 $1, 1, 3$ -trimethylcyclohexane 136.63	27	2,3,4 - trimethylpentane	113 47
281-methyl-cis-3-ethylcyclopentane121.521-methyl-1-ethylcyclopentane121.40291-trans-2-dimethylcyclohexane30n-octane31 $\begin{cases} 1, 3 - dimethylcyclohexane \\ 1, 4 - dimethylcyclohexane \\ 122.0032octene-1332, 2, 4-trimethylhexane \\ 1-cis-2-dimethylcyclohexane \\ 122.00342, 3, 5-trimethylhexane \\ 131.34351-cis-2-dimethylcyclohexane \\ 122.0036\begin{cases} 2-ethylhexene \\ octene-2 \\ 0 \\ ctene-2 \\ 125.6 \\ 136.19 \\ 1.1.3-trimethylcyclohexane \\ 136.63 \\ 136.6$		(3-methylhentane	118 19
$1 - methyl - l - ethyl cyclopentane121.321 - methyl - l - ethyl cyclopentane121.40291 - trans - 2 - dimethyl cyclohexane123.4230n - octane125.67311, 3 - dimethyl cyclohexane120.901, 4 - dimethyl cyclohexane118.3532octene - 1122.00332, 2, 4 - trimethyl hexane126.54342, 3, 5 - trimethyl hexane131.34351 - cis - 2 - dimethyl cyclohexane129.73362 - ethyl hexane120.00octene - 2125.637ethyl benzene136.19381 \cdot 1, 3 - trimethyl cyclohexane136.63$	28	1-methyl-cis-3-ethylcyclopentane	121 52
291-trans-2-dimethylcyclopentune121:4030n-octane123.4230n-octane125.6731 $\begin{cases} 1,3 - \text{dimethylcyclohexane} \\ 1,4 - \text{dimethylcyclohexane} \\ 18.35 \end{cases}$ 120.9032octene-1122.00332,2,4-trimethylhexane126.54342,3,5-trimethylhexane131.34351-cis-2-dimethylcyclohexane129.7336 $\begin{cases} 2-\text{ethylhexene} \\ \text{octene-2} \\ \end{cases}$ 126.5437ethylbenzene126.54381.1.3-trimethylcyclohexane136.19		1-methyl-l-ethylcyclopentane	121.52
1212121230n-octane125.6731 $\begin{cases} 1, 3 - \text{dimethylcyclohexane} \\ 1, 4 - \text{dimethylcyclohexane} \\ 1, 4 - \text{dimethylcyclohexane} \\ 122.0032octene-1122.00332, 2, 4-trimethylhexane126.54342, 3, 5-trimethylhexane131.34351-cis-2-dimethylcyclohexane129.7336\begin{cases} 2-\text{ethylhexene} \\ \text{octene-2} \end{cases}125.637ethylbenzene136.19381.1.3-trimethylcyclohexane136.63$	29	1-trans-2-dimethylcyclohevane	123 40
31 $\begin{cases} 1, 3 - \text{dimethylcyclohexane} \\ 1, 4 - \text{dimethylcyclohexane} \\$	30	n-octane	125.42
31 $1, 4$ - dimethylcyclohexane 118.35 32 octene-1 122.00 33 $2, 2, 4$ -trimethylhexane 126.54 34 $2, 3, 5$ -trimethylhexane 131.34 35 1 -cis-2-dimethylcyclohexane 129.73 36 2 -ethylhexene 120.00 $octene-2$ 125.6 37 ethylbenzene 136.19 38 $1.1.3$ -trimethylcyclohexane 136.63	50	(1, 3 - dimethylcyclohexane)	120.90
32octene-1122.0033 $2, 2, 4$ -trimethylhexane126.5434 $2, 3, 5$ -trimethylhexane131.3435 1 -cis-2-dimethylcyclohexane129.7336 2 -ethylhexene octene-2120.0037ethylbenzene136.1938 $1.1.3$ -trimethylcyclohexane136.63	31	1.4 - dimethylcyclohexane	118 35
33 $2, 2, 4-trimethylhexane$ 122.00 33 $2, 2, 4-trimethylhexane$ 126.54 34 $2, 3, 5-trimethylhexane$ 131.34 35 $1-cis-2-dimethylcyclohexane$ 129.73 36 $2-ethylhexene$ 120.00 $octene-2$ 125.6 37 ethylbenzene 136.19 38 $1.1.3-trimethylcyclohexane$ 136.63	32	octene-1	122 00
34 $2,3,5-trimethylnextile120.34342,3,5-trimethylnextile131.34351-cis-2-dimethylcyclohexane129.73362-ethylhexene120.00octene-2125.637ethylbenzene136.19381.1.3-trimethylcyclohexane136.63$	33	2.2.4-trimethylbeyane	126 54
$\begin{array}{cccc} 35 & 1-cis-2-dimethylackane & 129.73 \\ 36 & \begin{cases} 2-ethylhexene & 120.00 \\ octene-2 & 125.6 \\ 37 & ethylbenzene & 136.19 \\ 38 & 1.1.3-trimethylcyclohexane & 136.63 \\ \end{array}$	34	2,2,3 trimethylhexane	131 34
$\begin{array}{c} 36\\ 36\\ 37\\ 38\\ 38\\ 38\\ 38\\ 38\\ 38\\ 38\\ 38\\ 38\\ 38$	35	1-cis-2-dimethylcyclohexane	170 73
30 120.00 0ctene-2 125.6 37 ethylbenzene 136.19 38 1.1.3-trimethylcyclohexane 136.63	22 20	(2-ethylhexene	120.00
37ethylbenzene136.19381.1.3-trimethylcyclohexane136.63	30	octene-2	125.00 125 K
38 1.1.3-trimethylcyclohexane 136.63	37	ethylbenzene	136 10
	38	1.1.3-trimethylcyclohexane	136.63

TABLE III Cont'd

Peak No.	Component	B.P. (^O C)
30	(m-xylene	139.1
59	{p-xylene	138.35
40	2,3 - dimethylheptane	140.5
40	3,4 - dimethylheptane	140.6
	2,2,4 - trimethylheptane	147.88
41	$\langle 2, 2, 5 - trimethylheptane$	148
	2,2,6 - trimethylheptane	148.2
42	o-xylene	144.41
	(2-methyloctane	143.26
43	3-methyloctane	144.18
	4-methyloctane	142.48
44	n-nonane	150.8
45	isopropylbenzene (cumene)	152.39
	(2,3,5 - trimethylheptane	157.0
46	$\langle 2, 4, 5 - trimethylheptane$	157.0
	3.3.5 - trimethylheptane	155.68
47	nonene-1	146.0
48	unidentified oxygen or sulphur compound	
49	2.2.3.3-tetramethylbexane	160.31
50	2 6-dimethyloctane	158 54
51	$n_{\rm propyllogram} + 2$ 6-dimethyl-1-octope (tr)	150.04
52	2 6-dimethyl-l-octane	158 5
53	1-methyl-3-ethylbenzono	161 21
55	(1-methy1-4-ethy1benzone	161 00
54	p-cymane (isopropyltolyane)	176 0
	$(3 3 4 \pm trimethylboptano$	164
55	3 / 4-trimothylhoptapo	164
50	3 4 5-trimethylhoptane	164
56	(2-methylnonano	166 8
50	mositulono	162 166
57	1-methy1-2-ethy1bonzono	165 15
57	(1, 3, 5 + trimethylbenzene)	164 72
58	1 2 4-trimethylbongone	160 25
50	unidentified Creativelate	109.33
60		174 10
00	$\left(1, 2, 3-\text{trimothylbongono}\right)$	176 09
61	1-methyl-/-isopropylhonzono	177 10
	(1-methyl-2-icopropylbenzene	179 15
62	lindano	177
62		170 6
64		120.05
65	n-bulyicycionexane	180.95
66	unidentified C11 alkylate	
00	(n hutul hereene	100 07
67	1 4 dimothul 2 othulhor and	186.01
60*	(1,4-ulmelly1-2-elly1Denzene	107./
60%	J-methyldecane	100 C
07^ 70*	4-methyldecane	100
70*	z-metnyraecane	TAO

TABLE III Cont'd

Peak No.	Component		B.P. (^O C)
71*	3-methylundecane	• . •	192.1
72	n-undecane		195.89
73	unidentified methyl C ₁₁ alkylate		
74	isopentylbenzene		198.9
75	n-pentylbenzene		205.46
76	1,3-dimethy1-5-tert-buty1benzene		205.1
77	unidentified C_{12} alkylate		-
78	dodecane		216.78
79	1-dodecene		213
80	tridecene		235.44

* include traces of the following isomers:

1,4-dimethyl-2-ethylbenzene	190.01
1,3-dimethyl-4-ethykbenzene	188.41
1,2-dimethyl-4-ethylbenzene	189.75

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- Speeding up the procedure by using a totally chromatographic method. This would involve
 - (a) Replacing the distillation of the light oil from the hydrocracked product, by a simulated chromatographic distillation and collecting the naphtha sample covering the C_5 to C_{13} range.
 - (b) Using selective chemical absorption and flame ionization detection to separate and quantitatively collect the saturates, olefins and aromatic fractions of the naphtha sample. This chromatographic technique would replace the FIA micropreparative step.
 - (c) Determination of total sulphur content of the different hydrocarbon types or peaks by a flame photometric detector on the line instead of taking the sample to a separate apparatus for that purpose. This would allow sulphur determination in extremely small hydrocarbon fractions that could not be determined otherwise.
- 2. Quantitative determination of the main peaks on the chromatogram as well as the main hydrocarbon types present in the sample, using the integration and data stream systems.



KOVAT'S INDICES AND COMPOUND IDENTIFICATION

(CAP.G.C., QUADRUPOLE M.S., COMPUTER)

SEPARATION AND IDENTIFICATION SCHEMATIC





MICRO-PREPARATIVE FIA CHROMATOGRAPHIC SYSTEM



CHROMATOGRAM OF NAPHTHA FRACTION OF HYDROCRACKED ATHABASCA BITUMEN