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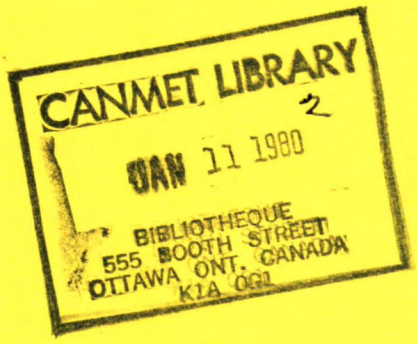

RAPID CHROMATOGRAPHIC PROCEDURE FOR CHARACTERIZING HYDROCARBONS IN SYNTHETIC FUEL NAPHTHA

A.E. GEORGE, G.T. SMILEY AND H. SAWATZKY

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RAPID CHROMATOGRAPHIC PROCEDURE FOR CHARACTERIZING HYDROCARBONS IN SYNTHETIC FUEL NAPHTHA

by

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

ABSTRACT

A procedure for the chemical characterization of hydrocarbons in the naphtha fraction C_5 to C_{13} from synthetic fuels has been developed. The procedure provides complete distillation information, sulphur content, hydrocarbon-type distribution analysis of saturates, olefins and aromatics as well as individual identification of the major hydrocarbon constituents of the naphtha. The method employs gas chromatography, selective chemical absorption, and both flame ionization and flame photometric detection. Quadrupole mass spectrometer interfaced with integration and data analysis system was used for identification of the individual hydrocarbons.

A complete characterization takes 90 min. and requires only 30 µL of sample. The results of hydrocarbon-type distribution are not dependent upon interpretation by the analyst as in the standard fluorescent indicator adsorption method. The flame photometric sulphur detection was preceded by chromatographic separation, and its flow parameters were modified to meet the high sulphur requirement of the naphthas from synthetic fuels.

Five naphtha samples produced by the hydrocracking of Athabasca bitumen under various operating conditions were analyzed by this method.

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PROCEDE CHROMATOGRAPHIQUE RAPIDE POUR LA CARACTERISATION DES HYDROCARBURES DANS LE CARBURANT DE NAPHTA SYNTHETIQUE

par

A.E. George*, G.T. Smiley** et H. Sawatzky***

RESUME

Une technique a été mise au point dans le but de caractériser les hydrocarbures de C_5 à C_{13} dans une fraction de naphta des combustibles synthétiques. Cette méthode permet d'obtenir les renseignements complets sur la distillation, la teneur en soufre, l'analyse de la distribution type d'hydrocarbures saturés, oléfiniques et aromatiques ainsi que l'identification des hydrocarbures les plus abondants dans le naphta. La méthode fait appel à la chromatographie en phase gazeuse basée sur l'absorption chimique sélective et utilisant la détection par ionisation de flamme et photométrie de flamme. L'identification des hydrocarbures est effectuée en utilisant un spectromètre de masse quadrupolaire couplé à un intégrateur et un système d'analyse des données.

Une analyse complète requiert 30 µL d'échantillon et dure environ 90 min. Les résultats de la distribution type en hydrocarbone ne dépendent plus de l'interprétation par le technicien comme c'est le cas pour la méthode standard d'absorption par indicateur fluorescent. La détection du soufre par photométrie de flamme est précédée d'une séparation par chromatographie et ses paramètres de débit sont modifiés afin de respecter les exigences en teneur de soufre élevé des naphtas provenant des carburants synthétiques.

Cinq échantillons de naphta obtenus par hydrocraquage du bitume d'Athabasca selon différentes conditions expérimentales, sont analysés par cette méthode.

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* Chef intérimaire de la Section et ** Technicien, Section de la recherche sur les substances bitumineuses, Laboratoire de recherche sur les combustibles sythétiques, Laboratoires de recherche sur l'Energie, *** Directeur adjoint, Transformation, Bureau des programmes de recherche sur l'Energie, CANMET, Energie, Mines et Ressources Canada, Ottawa.

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INTRODUCTION

The need for a rapid method to determine the hydrocarbon component composition of full range naphtha in synthetic fuels has been evident since Energy Research Laboratories started pilot plant investigations of hydrocracking. Fast characterization of products is needed to monitor the effect of altering process conditions to meet certain product quality requirements.

A previously reported procedure for this purpose involved distillation of the light oil product followed by separation of the saturated, olefinic and aromatic hydrocarbon fractions on a micropreparative silica column using the fluorescent indicator adsorption (FIA) principle (1). A gas chromatography-quadrupole mass spectrometric system was employed for component identification. This report describes further development and improvement of the procedure.

The procedure has been made simpler and faster by developing an entirely gas chromatographic method involving the following steps:

1. Replacing the distillation of light oil product by simulated chromatographic distillation and collecting the naphtha fraction from C_5 to C_{13}.
2. Using selective chemical absorption and flame ionization (FID) to determine the saturates, olefins and aromatics content of the naphtha sample. This chromatographic technique replaces the FIA technique.
3. Determining sulphur content of the naphtha sample by using a flame photometric detector on-line instead of taking the sample to a separate apparatus for that purpose; this allows sulphur determination in extremely small hydrocarbon fractions that could not otherwise be analyzed.

The main peaks in the chromatogram and the main hydrocarbon types present in the sample are determined quantitatively using integration and data analysis systems.

EXPERIMENTAL

A schematic diagram of the separation and identification procedure is shown in Fig. 1.

HYDROCRACKING

Hydrocracking of Athabasca bitumen from Great Canadian Oil Sands was carried out in a 159 L/day pilot plant (Table 1). The operating details have been described elsewhere (2).

Table 1 - Properties of Athabasca bitumen

Property	Value
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

SAMPLES FOR ANALYSIS

The following samples were subjected to gas chromatography:

- Fifty-four individual petroleum hydrocarbons, including straight-chain and branched alkanes, cycloparaffins, olefins and aromatics (Table 2). These compounds were diluted by a factor of 50 with n-pentane before chromatography.
- Five light oil products from the hydrocracking of Athabasca bitumen under various processing conditions. These samples are designated 1 to 5 in Tables 3 and 4.

SIMULATED DISTILLATION

True boiling point data for a 30-µL sample of the light product of hydrocracked Athabasca bitumen were obtained automatically by

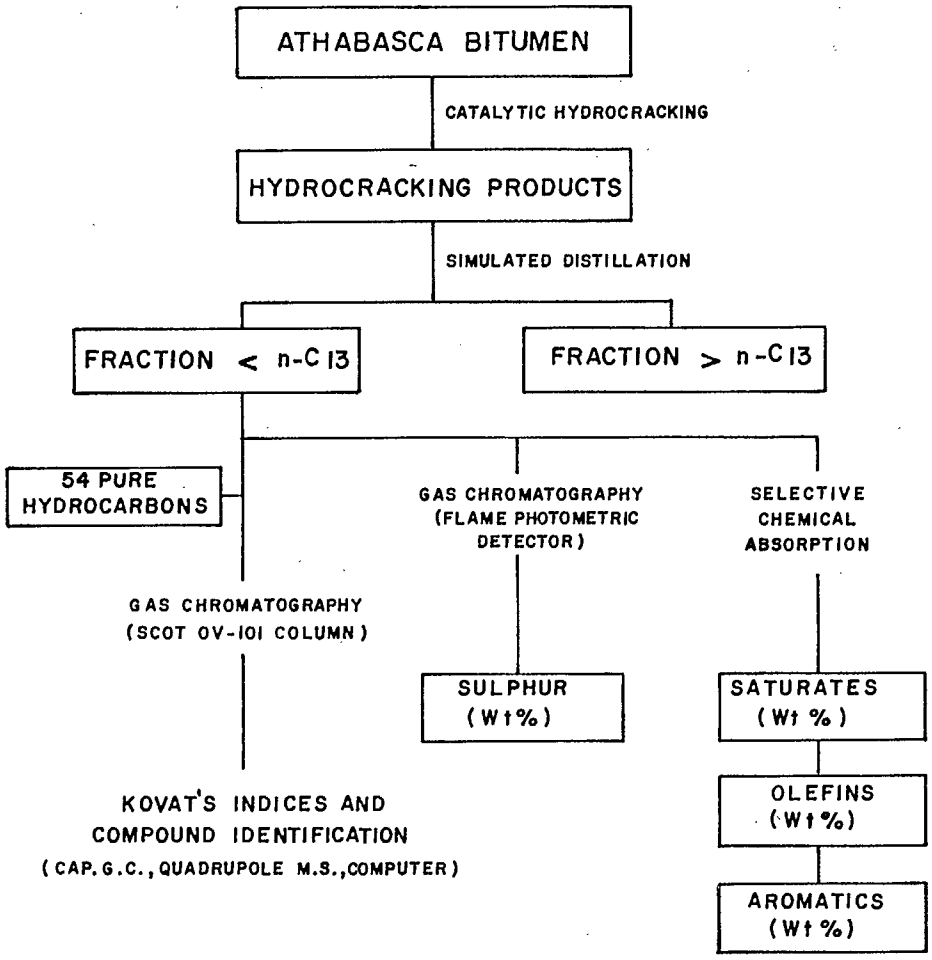

Fig. 1 - Separation and identification schematic

Athabasca bitumen were obtained automatically by gas chromatography as represented by G.C.1 in Fig. 2. A stainless steel column, 2500 mm x 3 mm OD, packed with 10% OV-101 on chromosorb W was used. The support material was acid-washed and treated with dimethyl dichlorosilane. The helium carrier gas flow was 4 0 mL/min. Other experimental details are as described by Green (3) and ASTM D2887-73.

The column effluent (naphtha fraction from C_5 to C_{13}) was split into three streams and collected simultaneously in three U-tube traps packed with chromosorb W. The traps were cooled in an acetone-dry ice bath and samples thus collected (Fig. 2).

The naphtha samples collected in traps 1, 2 and 3 were directed to an analytical SCOT column shown as G.C.2, selective chemical absorption (SCA) and to the chromatographic sulphur analysis column shown as G.C.3, respectively.

Table 2 - Kovat's retention indices (K.I.)
for reference hydrocarbon compounds

Compound	K.I.	Compound	K.I.
n-pentane	500	3-methylheptane	778.9
2,2-dimethylbutane	536.8	2,2,5-trimethylhexane	788.7
2,3-dimethylbutane	536.8	n-octane	800
2-pentene	536.8	octene-1	813.8
2-methylpentane	573.7	cis-1,2-dimethylcyclohexane	827.6
4-methylpentene-2 (cis + trans)	573.7	2-ethylhexene-1	832.2
4-methylpentene-1	584.2	octene-2	839.1
3-methylpentane	589.5	ethylbenzene	854.0
n-hexane	600	m-xylene	863.2
2-methylpentene-1	606.8	p-xylene	863.2
hexene-1	606.8	o-xylene	886.2
2-ethyl-butene-1	613.6	n-nonane	900
hexene-2	627.2	cumene	915.9
benzene	652.3	nonene-1	917.0
cyclohexane	656.8	p-cymene	951.1
2,3-dimethylpentane	665.9	mesitylene	964.8
3-methylhexane	675.0	n-decane	1000
2,2,4-trimethylpentane	688.6	decene-1	1017.9
n-heptane	700	n-propylbenzene	1021.4
heptene-1	711.3	n-butylbenzene	1051.2
methylcyclohexane	718.3	n-undecane	1100
heptene-3	719.7	n-dodecane	1200
heptene-2 (cis + trans)	726.8	n-hexylbenzene	1256.5
2,4-dimethylhexane	733.8	n-tridecane	1300
2,5-dimethylhexane	733.8	n-tetradecane	1400
2,3,4-trimethylpentane	749.3	n-octylbenzene	1467.2
toluene	759.2	n-pentadecane	1500

Table 3 - Determination by flame photometry
and X-ray fluorescence methods

	Sulphur content, wt %	
	X-ray fluorescence	Flame photometry *
1	0.87	0.86
2	0.32	0.34
3	0.84	0.83
4	1.57	1.56
5	1.80	1.80

* Precision is ±0.003 on average of 10 determinations per sample.

Table 4 - Comparison of hydrocarbon-type analysis by the chemical absorption and fluorescent indicator absorption methods

Sample	Saturates wt %	Olefins wt %	Aromatics wt %
1 - A*	52.0	35.2	12.8
- B*	52.2	35.1	12.7
2 - A	58.7	26.0	15.3
- B	58.6	25.9	15.5
3 - A	47.2	39.5	13.3
- B	46.9	39.7	13.4
4 - A	38.9	43.1	18.8
- B	38.0	43.3	18.7
5 - A	35.9	42.2	21.9
- B	35.8	42.4	21.8

(*) A - determined by selective chemical absorption (SCA)

B - determined by fluorescent indicator absorption (FIA).

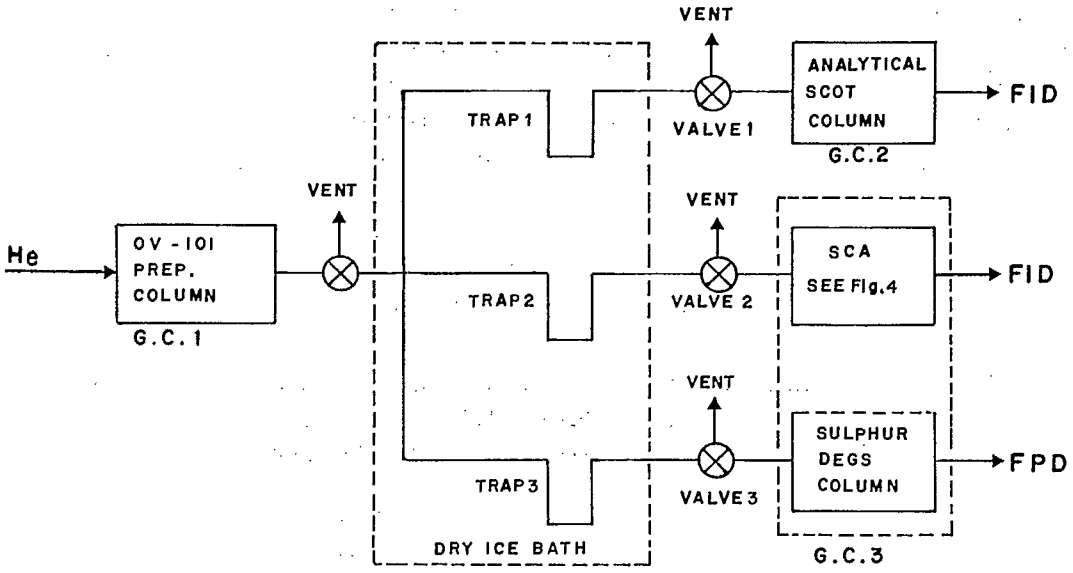

Fig. 2 - Chromatographic system for naphtha analysis

SULPHUR ANALYSIS

The naphtha fraction from C_5 to C_{13} in trap 3 in Fig. 2 was directed in G.C.3 and analyzed for sulphur using a flame photometric detector (5).

A Microtek MT-220 gas chromatograph equipped with a Melpar flame photometric detector was used. A stainless steel column 2500 mm x 3 mm OD packed with 10% diethylene glycol succinate (DEGS) on chromasorb W was used. Helium was used as a carrier gas at a flow rate of 65 mL/min. A column temperature of 110°C was adequate for separation. Both the injection port and the detector were maintained at a temperature of 170°C. The hydrogen and oxygen flow rates in the detector were maintained at 10 and 40 mL/min. respectively. The detector output was monitored using a 1 mV strip-chart recorder and a Spectra-Physics System I computing integrator.

All solvents and reagents were +99% gas chromatographically pure. Sulphur-free ethylbenzene was used as a solvent as well as in the blank experiments. Ethyl sulphide, diethyl sulphide and thiophene were used to obtain the calibration data shown in Fig. 3. Sample volumes up to 2.0 µL were analyzed in approximately 5 min.

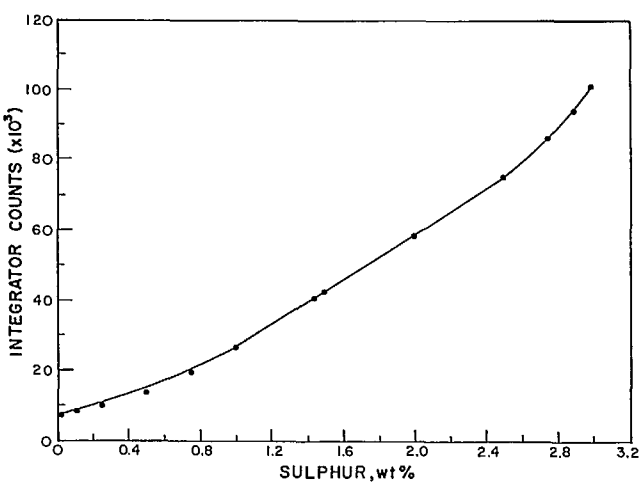

Fig. 3 - Calibration of the flame photometric detector

HYDROCARBON-TYPE SEPARATION

This was achieved by selective chemical absorption (SCA) shown in Fig. 2. The contents of trap 2 were heated and passed through a transfer line into the chemical absorption section as described previously (4). The sample was split into three equal fractions and passed through three columns (Fig. 4). The flow pattern of the SCA oven is shown schematically in Fig. 5.

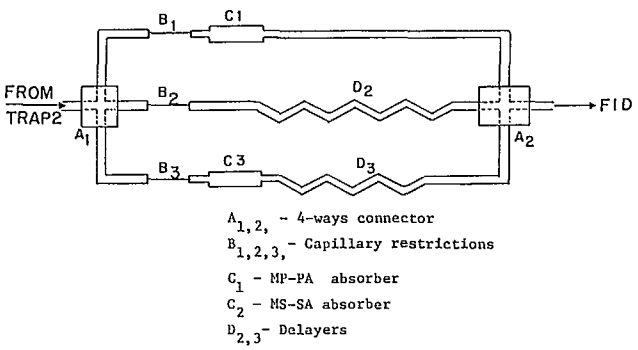

Fig. 4 - Selective chemical absorption analyzer

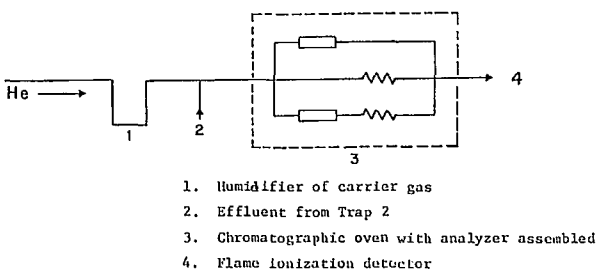

Fig. 5 - Flow diagram of selective chemical absorption analyzer

The experimental conditions were as follows:

Temperature (°C)	Absorbents: 70
	Humidifier: 20
Length of 0.1 mm ID capillaries (mm)	B_1: 90
	B_2: 170
	B_3: 90
Flow rate (mL/min)	Branch 1: 6.5
	Branch 2: 3.2
	Branch 3: 6.5

Delayers, size and volume

D_2: 10 mm x 2 mm, ID; 3.2 mL

D_3: 25 mm x 2.3 mm, ID; 10 mL

The different hydrocarbon types analyzed in the system elute in the following order.

Peak 1 - Saturated hydrocarbons from the mercuric perchlorate-perchloric acid absorber (MP-PA) where the aromatics and olefins were retained.

Peak 2 - Total sample from the column with no absorber.

Peak 3 - The saturated and aromatic hydrocarbons from the mercuric sulphate-sulphuric acid absorber (MS-SA) where the olefins were retained.

The hydrocarbon-type distribution was calculated as follows:

$$\text{Saturates wt \%} = \frac{\text{integrator count of peak 1}}{\text{integrator count of peak 2}} \times 100$$

$$\text{Aromatics wt \%} = \frac{\text{int count peak 3 - peak 1}}{\text{int count peak 2}} \times 100$$

Olefins wt % was obtained by difference.

The mean density of the aromatic fraction was estimated as 0.87 and the saturate and olefins fractions at 0.67. The FIA results are usually reported in volume per cent. Applying the density factors allowed comparison to be made with the FID response results on a weight per cent basis, as shown in Table 4.

GAS CHROMATOGRAPHY - MASS SPECTROMETRY (GC-MS) OF TOTAL NAPHTHA

The naphtha sample collected in trap 1 was directed through valve 1 to the SCOT column G.C.2, Fig. 2 and chromatographed as described in an earlier report (1).

Mass spectral analyses were performed using a Finnigan 4000 gas chromatograph-quadrupole mass spectrometer interfaced with an Incos Nova 3 computer. A SCOT capillary column coated with OV-101 and conditioned as above was used for the analyses.

RESULTS AND DISCUSSION

In the relatively rapid analytical procedure there was no attempt made to perform high resolution chromatographic separation; only the major hydrocarbon components were identified. The compound-type distributions of the nitrogenous and sulphurous components have been reported before (6,7).

PURE PETROLEUM HYDROCARBONS

Retention data for the 54 pure petroleum hydrocarbons chromatographed in the system are shown in Table 2 expressed as Kovat's Indices. These hydrocarbons range in boiling points from 36 to 270°C, which adequately covers the naphtha boiling range and allows for the incorporation of material boiling higher than 200°C in distillation. The elution of these hydrocarbons from C_5 to C_{15} on the SCOT column coated with OV-101 is linear relative to their boiling points (Fig. 6).

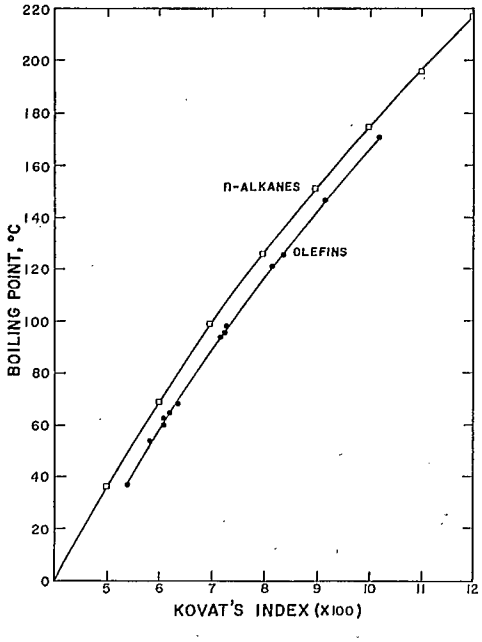

Fig. 6 - Retention data of hydrocarbons on SCOT column

NAPHTHA FROM HYDROCRACKING

Characteristics of the naphtha product employed in this procedure are given in Table 5.

Table 5 - Chemical characteristics of the hydrocracked naphtha fraction used for GC/MS analysis

Property	Value
Boiling range, °C	<200
Sulphur, wt %	0.32
Nitrogen, wt %	0.10
Saturates, vol %	67.4
Olefins, vol %	22.1
Aromatics, vol %	10.5

The chain and cyclic alkanes constitute 67.4% of the sample. The olefinic content is also relatively high at 22.1%, reflecting the cracking conditions to which the bitumen had been subjected in the pilot plant.

DISTILLATION DATA

The C_5 to C_{13} true boiling point range was separated by simulated distillation in about 10 min. The chromatogram provides distillation information at any given boiling point or distillation yield.

TOTAL SULPHUR CONTENT

Clay's technique was modified by replacing the gas mixing device with a chromatographic column (5). This enabled separation of a large portion of the non-sulphurous material from the sulphur-containing components, thereby reducing the contribution of non-sulphur-containing compounds to the flame photometric response (Fig. 7). Chromatographic separation reduces the total amount of sulphur species entering the flame at a given time. This, as well as the detector flow parameters chosen, extended the usable range of detection from 0.002 to 3.00 wt % sulphur. This feature is necessary for analyzing synthetic fuels naphtha as they have relatively high sulphur contents.

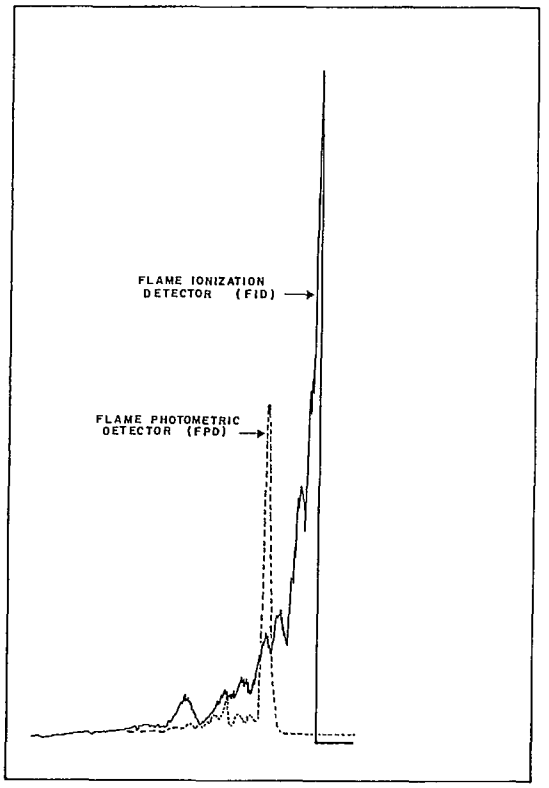

Fig. 7 - Separation of the sulphur components on the DEGS column

Five naphtha products from hydrocracked Athabasca bitumen were used to test the system. Comparison of results with the sulphur contents determined by X-ray fluorescence (INAX) shows close agreement (Table 3).

HYDROCARBON-TYPE ANALYSIS

Separation of the hydrocarbon types, integration of peaks and calculations were done automatically in about 20 min. This is considerably faster than the FIA analysis which also requires a much larger sample size, the use of solvents and is highly dependent on interpretation by the analyst as percentages of types are determined by manual measurement of the bands.

The hydrocarbon-type distribution in the five naphtha products as determined by both chromatographic chemical absorption and FIA is shown in Table 4.

INDIVIDUAL HYDROCARBON IDENTIFICATION

Individual peaks were identified from the chromatography of the total naphtha product on the SCOT column using the quadrupole mass spectrometer and data system. It was possible to identify 106 different hydrocarbon compounds in the 80 resolved peaks from the naphtha chromatogram (Table 6) (Fig. 8). This represents 97% by volume of the total naphtha fraction.

Table 6 - Hydrocarbon components identified in the naphtha fraction of hydrocracked Athabasca bitumen

Peak No.	Components	B.P. (°C)
1	isobutane	- 11.73
2	butene-1	- 6.26
3	butane	- 0.50
4	pentene-1	29.97
5	n-pentane	36.07
6	cis-2-pentene	36.94
	trans-2-pentene	36.35
7	cyclopentane	44.24
8	2,2-dimethylbutane	49.74
9	4-methyl-pentene-1	53.88
10	2-methyl-2-pentene	67.70
11	n-hexane	68.74
12	cis-2-hexene	68.84
	trans-2-hexene	67.87
13	1-methyl-1-cyclopentene	72
14	3-methyl-trans-2-pentene	70.44
15	methylcyclopentane	71.81
16	benzene	80.10
17	cyclohexane	80.74
18	3-methyl-hexane	91.85
19	cis-1,3-dimethylcyclopentane	91.73
20	n-heptane	98.43
21	heptene-2	98.50
22	methylcyclohexane	100.93
23	ethylcyclopentane	103.47
24	2-methyl-3-ethylpentane	115.65
25	2,2,3-trimethylpentane	109.84
26	toluene	110.63
27	2,3,3-trimethylpentane	114.76
	2,3,4-trimethylpentane	113.47
28	3-methylheptane	118.19
	1-methyl-cis-3-ethylcyclopentane	121.52
	1-methyl-1-ethylcyclopentane	121.40
29	1-trans-2-dimethylcyclohexane	123.42

Table 6 (Cont'd)

Peak No.	Components	B.P. (°C)
30	n-octane	125.67
31	1-3-dimethylcyclohexane	120.90
	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
39	m-xylene	139.1
	p-xylene	138.35
40	2,3-dimethylheptane	140.5
	3,4-dimethylheptane	140.6
	2,2,4-trimethylheptane	147.88
41	2,2,5-trimethylheptane	148
	2,2,6-trimethylheptane	148.2
42	o-xylene	144.41
43	2-methyloctane	143.26
	3-methyloctane	144.18
	4-methyloctane	142.48
44	n-nonane	150.8
45	isopropylbenzene (cumene)	152.39
46	2,3,5-trimethylheptane	157.0
	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-tetramethylhexane	160.31
50	2,5-dimethyloctane	158.54
51	n-propylbenzene + 2,6-dimethyl-1-octene (tr)	159.22
52	2,6-dimethyl-1-octene	158.5
53	1-methyl-3-ethylbenzene	161.31
54	1-methyl-4-ethylbenzene	161.99
	p-cymene (isopropyltoluene)	176.0
55	3,3,4-trimethylheptane	164
	3,4,4-trimethylheptane	164
	3,4,5-trimethylheptane	164
56	2-methylnonane	166.8
	mesitylene	163-166
57	1-methyl-2-ethylbenzene	165.15

Table 6 (Cont'd)

Peak No.	Components	B.P. (°C)
58	1,3,5-trimethylbenzene	164.72
	1,2,4-trimethylbenzene	169.35
59	unidentified C_{10} alkylate	-
60	n-decane	174.12
61	1,2,3-trimethylbenzene	176.08
	1-methyl-4-isopropylbenzene	177.10
62	1-methyl-2-isopropylbenzene	178.15
	indane	177
63	1-decene	170.6
64	n-butylcyclohexane	180.95
65	unidentified C_{11} alkylate	-
66	unidentified C_{11} aklylate	-
67	n-butyl benzene	183.27
	1,4-dimethyl-2-ethylbenzene	186.91
68*	5-methyldecane	187.4
69*	4-methyldecane	188.6
70*	2-methyldecane	190
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-dimethyl-5-tert-butylbenzene	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-ethylbenzene	188.41
1,2-dimethyl-4-ethylbenzene	189.75

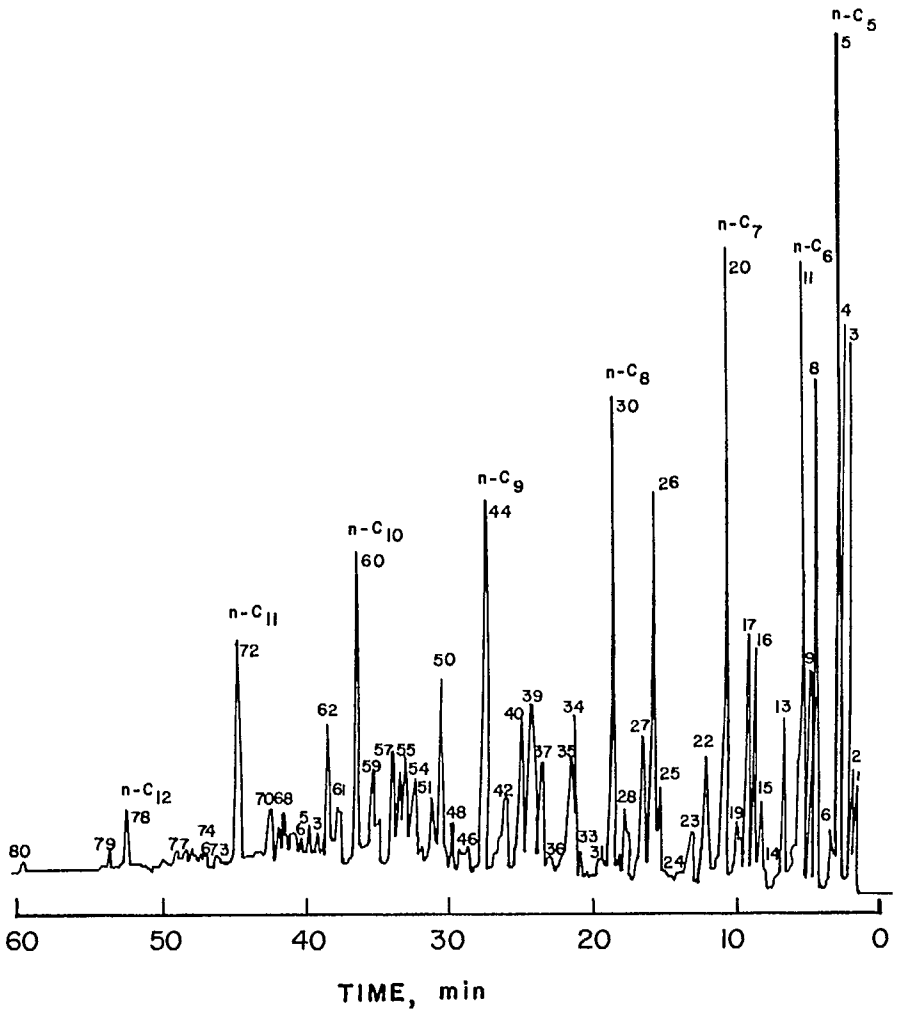

Fig. 8 - Chromatogram of naphtha fraction of hydrocracked Athabasca bitumen

CONCLUSIONS

A rapid chromatographic procedure has been developed for chemical characterization of the naphtha fraction of synthetic fuels. The procedure involves chromatographic separation of the naphtha boiling range C_5 to C_{13}, sulphur analysis, hydrocarbon-type distribution analysis of saturates, olefins and aromatics and individual hydrocarbon identification. Mass spectrometry was coupled to gas chromatography in the latter. A complete characterization takes 90 min/sample.

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