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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 barrèl 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°C. 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 hydrocarbon-type 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^oC per minute starting at room temperature up to 175^oC; holding at this temperature for 6 hours; programming up to 250^oC at 1^oC per minute; holding for 30 minutes turning the heater off and allowing the column to cool to 100^oC. The column temperature was maintained at 100^oC overnight. This column conditioning technique proved most successful in reducing column bleed, particularly in mass spectral analyses. The injection system was maintained at 210^oC and the detector at 310^oC. After the gas chromatograph reached an equilibrium temperature of 40^oC, a 1.2 μ l sample was injected. The column was held at 40^oC for 5 minutes and then programmed at 2^oC per minute to 170^oC. Retention data from at least five reproducible chromatograms were used to calculate the Kovat's Index for each compound.

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 Athabasca 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, iso-alkanes, 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 hydrocarbon-type 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, °C	-200
Sulphur, wt %	0.32
Nitrogen, wt %	0.10
Saturates, vol %	67.4
Olefins, vol %	22.1
Aromatics, vol %	10.5

TABLE II

Kovat's Retention Indices for Reference Hydrocarbon Compounds

Compound	K. I.
n-Pentane	500
2,2 - dimethylbutane	536.8
2,3 - dimethylbutane	536.8
2 - pentene	536.8
2 - methylpentane	573.7
4 - methylpentene-2 (cis + trans)	573.7
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 - methylhexane	675.0
2,2,4 - trimethylpentane	688.6
n-Heptane	700
Heptene-1	711.3
Methylcyclohexane	718.3
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 - methylheptane	778.9
2,2,5 - trimethylhexane	788.7
n-Octane	800
Octene-1	813.8
cis - 1,2 - dimethylcyclohexane	827.6
2 - ethylhexene-1	832.2
Octene-2	839.1
Ethylbenzene	854.0
m-xylene	863.2
p-xylene	863.2
o-xylene	886.2
n-Nonane	900
Cumene	915.9
Nonene-1	917.0
p-cymene	951.1
Mesitylene	964.8
n-Decane	1000
Decene-1	1017.9

TABLE II Cont'd

Compound	K.I.
n-Propylbenzene	1021.4
n-Butylbenzene	1051.2
n-Undecane	1100
n-Dodecane	1200
n-Hexylbenzene	1256.5
n-Tridecane	1300
n-Tetradecane	1400
n-Octylbenzene	1467.2
n-Pentadecane	1500

TABLE III

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

Peak No.	Component	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	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-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
	{ 3-methylheptane	118.19
28	{ 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	{ 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

TABLE III Cont'd

Peak No.	Component	B.P. (°C)
39	{ m-xylene	139.1
	{ p-xylene	138.35
40	{ 2,3 - dimethylheptane	140.5
	{ 3,4 - dimethylheptane	140.6
41	{ 2,2,4 - trimethylheptane	147.88
	{ 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	2,6-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
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 alkylate	-
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

TABLE III Cont'd

Peak No.	Component	B.P. (°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-dimethyl-5-tert-butylbenzene	205.1
77	unidentified C ₁₂ alkylate	-
78	dodecane	216.78
79	1-dodecene	213
80	tridecene	235.44

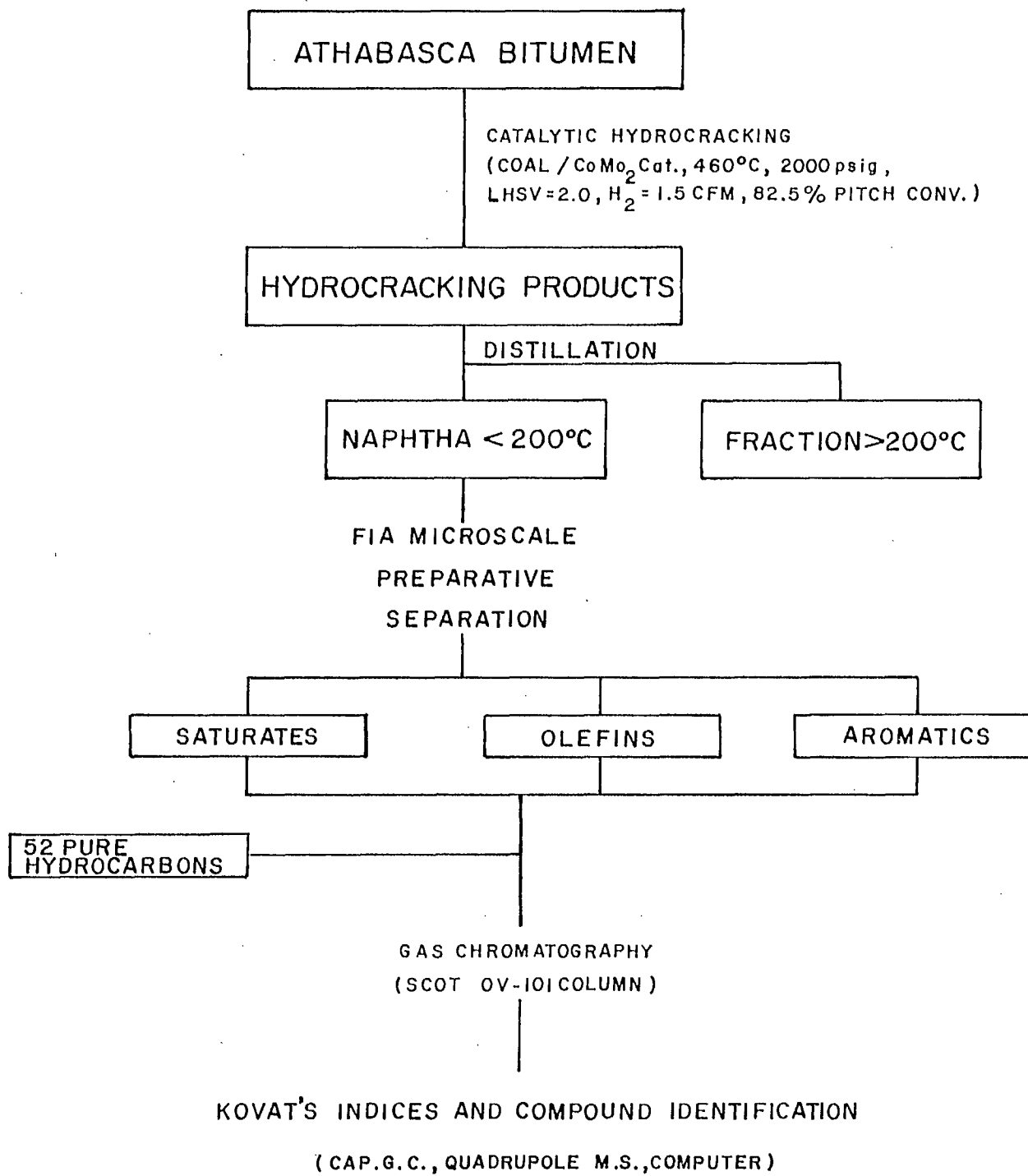
* include traces of the following isomers:

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

SUGGESTIONS FOR FURTHER WORK

1. 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 C₅ to C₁₃ 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.



SEPARATION AND IDENTIFICATION SCHEMATIC

FIGURE 1

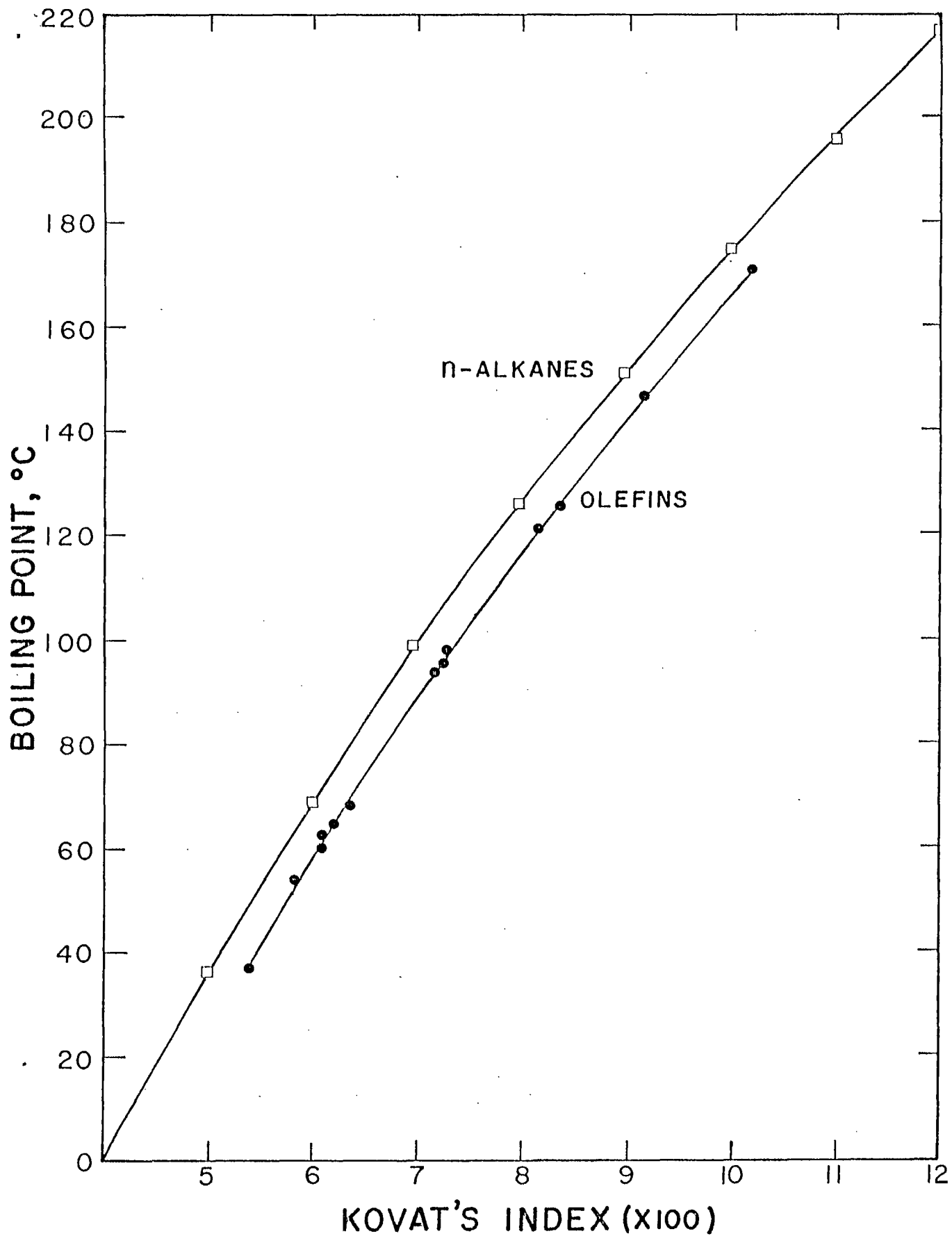
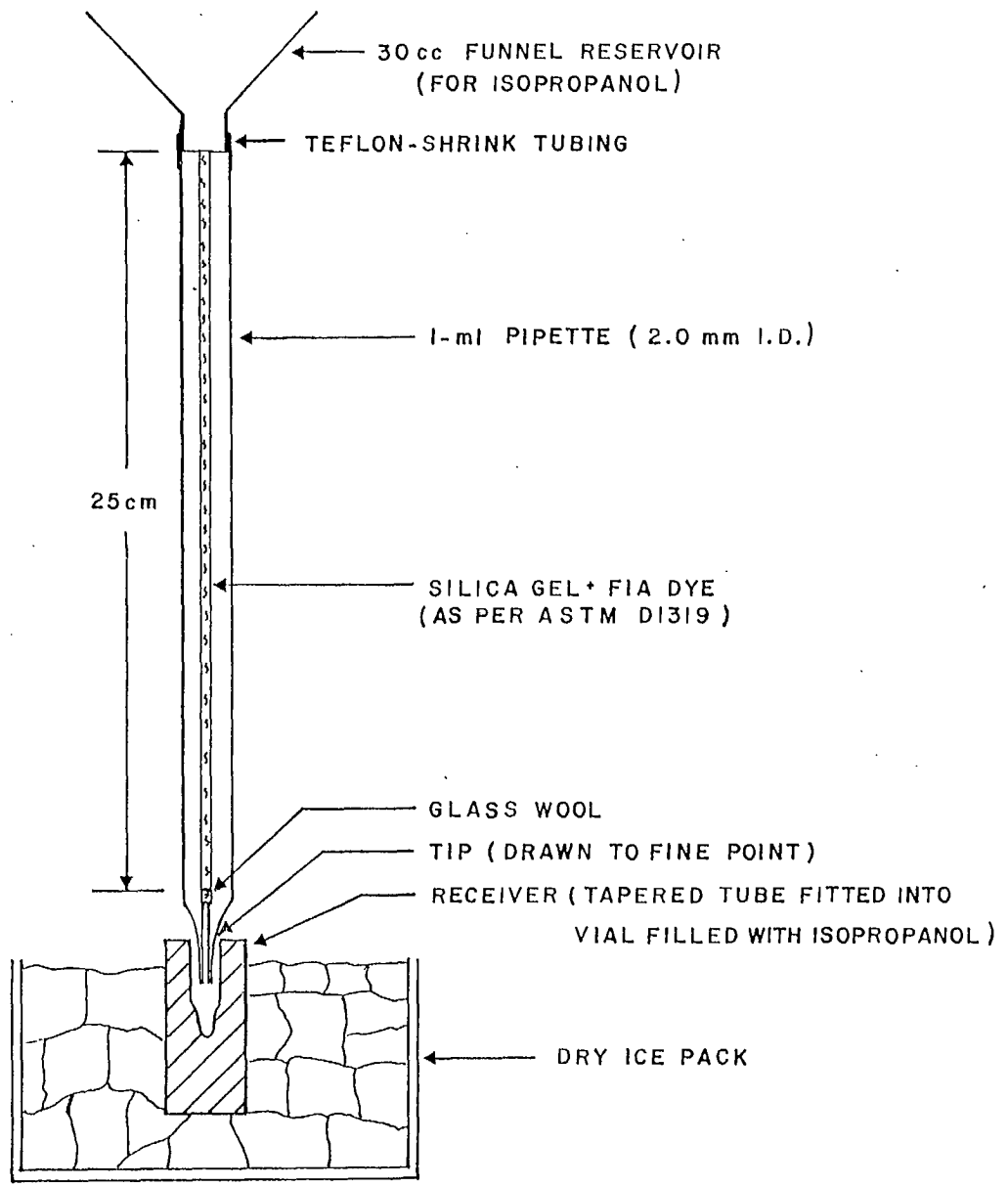
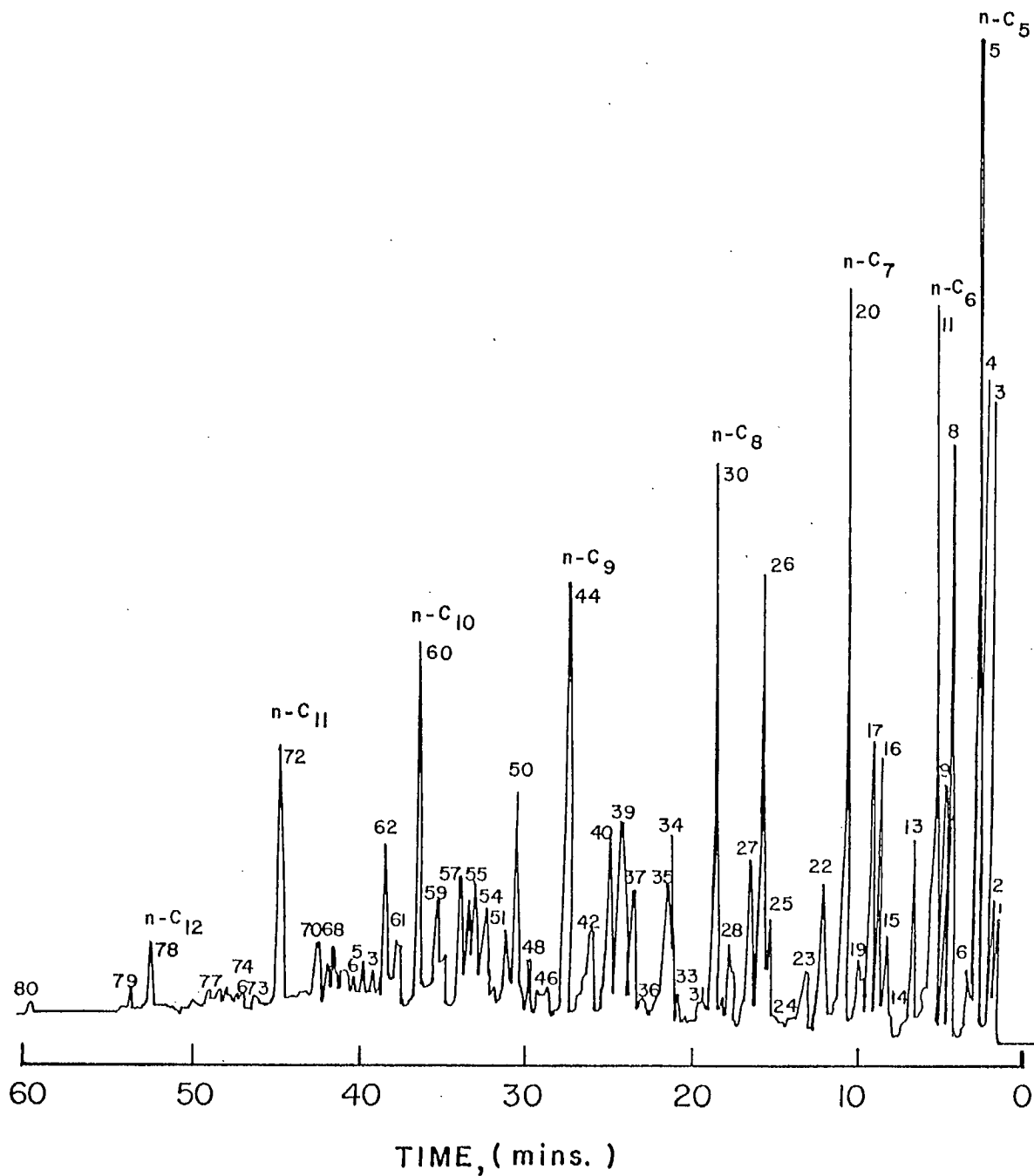


FIGURE 2



MICRO-PREPARATIVE FIA CHROMATOGRAPHIC SYSTEM

FIGURE 3



**CHROMATOGRAM OF NAPHTHA FRACTION OF
HYDROCRACKED ATHABASCA BITUMEN**

FIGURE 4