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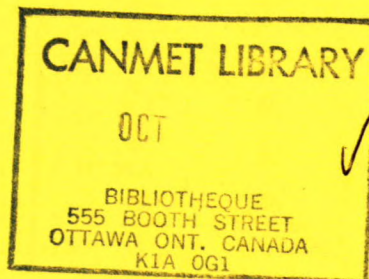
REPORT 81-5E

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HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC HPLC METHOD FOR TYPE ANALYSIS OF HYDROCARBONS IN SYNTHETIC FUEL NAPHTA

J.E. BESHAI AND A.E. GEORGE



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HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC HPLC METHOD FOR TYPE
ANALYSIS OF HYDROCARBONS IN SYNTHETIC FUEL NAPHTHA

by

J.E. Beshai* and A.E. George**

ABSTRACT

A rapid method has been developed which provides type distribution analysis of the saturated, olefinic and aromatic hydrocarbons in the naphtha fraction (IBP - 200°C). The method employs a dual-column high pressure liquid chromatography (HPLC) system of μ -Porasil and diamine bonded phase sorbents with n-hexane as a mobile phase.

A complete characterization takes 20 min and requires only 2.5 μ L of sample. The results are not dependent on interpretation by the analyst as in the Standard Fluorescent Indicator Adsorption (FIA) method. It is also more suitable for naphthas from synthetic fuels because they usually contain considerably higher amounts of olefinic hydrocarbons. Separations are reproducible and the separated fractions are suitable for further analysis. The method could also be automated and the results reported in a printout.

A number of naphtha samples produced by the hydrocracking of Cold Lake bitumen and Lloydminster and Boscan heavy oils under various operating conditions were analyzed.

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MÉTHODE DE CHROMATOGRAPHIE À HAUT RENDEMENT PAR VOIE HUMIDE POUR
L'ANALYSE DES TYPES D'HYDROCARBURES DANS LE NAPHTHA SYNTHÉTIQUE

par

J.A. Beshai* and A.E. George**

RÉSUMÉ

Une méthode rapide a été mise au point pour analyser la distribution des types d'hydrocarbures saturés, oléfiniques et aromatiques dans la fraction de naphtha (P.E.I. 200°C). Cette méthode fait usage d'un système de chromatographie à haute pression par voie humide à deux colonnes dont l'une est remplie de μ -Parasil et l'autre de diamine avec le n-hexane comme phase mobile.

Une caractérisation complète prend 20 minutes et ne nécessite qu'un échantillon de 2,5 μ L. Les résultats ne dépendent pas de l'interprétation de l'analyste comme c'est le cas pour la méthode normalisée d'absorption par indicateur fluorescent. Cette méthode convient beaucoup plus aux naphthas provenant des carburants synthétiques puisque ceux-ci contiennent habituellement des quantités beaucoup plus importantes d'hydrocarbures oléfiniques. On peut reproduire les séparations et les fractions séparées peuvent subir d'autres analyses. Cette méthode pourrait aussi être informatisée ainsi les résultats apparaîtraient sur des imprimés.

On a analysé plusieurs échantillons de naphtha provenant de l'hydrocraquage, dans diverses conditions d'opération, du bitume de Cold Lake et des huiles lourdes de Lloydminster et de Boscan.

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CONTENTS

	<u>Page</u>
ABSTRACT	i
RESUMÉ	ii
INTRODUCTION	1
EXPERIMENTAL	1
Upgrading	1
Distillation	1
Analyzed Samples	1
Compound-type Separation	2
RESULTS AND DISCUSSION	2
Chromatography of the Model Hydrocarbons	3
Calculation of Hydrocarbon-type Content	3
Chromatography of Synthetic Fuel Naphthas	4
CONCLUSION	6
REFERENCES	6

TABLES

1. High performance liquid chromatographic separation of model hydrocarbon compounds	2
2. HPLC analysis of hydrocarbon standard mixture for saturates, olefins and aromatics	4
3. Hydrocarbon-type analysis of naphtha from Lloydminster processing products (comparison of FIA and HPLC methods) ..	4
4. Hydrocarbon-type analysis of naphtha from Cold Lake processing products using HPLC separation	6
5. Hydrocarbon-type analysis of naphtha from Boscan processing products using HPLC separation	6

FIGURES

1. Upgrading and separation schematic	1
2. Liquid chromatograph equipped with backflush	3
3. Chromatogram of standard sample mixture	5
4. Chromatogram of naphtha from Lloydminster hydrocracked product	5
5. Chromatogram of naphtha from Cold Lake hydrocracked product	5
6. Chromatogram of naphtha from Boscan hydrocracked product ..	5

INTRODUCTION

The need for a rapid method to determine the hydrocarbon-type composition of full range naphtha in synthetic fuels has been perceived since the Energy Research Laboratories first started pilot plant investigations for upgrading bitumens and heavy oils. Fast characterization of products is needed to monitor the effect of altering process parameters to meet certain product quality requirements.

The Standard Fluorescent Indicator Adsorption (FIA) method has been used for the analysis of hydrocarbon types in the naphtha fraction of petroleum and synthetic fuels (1). The hydrocarbons are separated into saturates, olefins and aromatics using a silica column under low pressure of less than 0.10 MPa with isopropyl alcohol as the mobile phase. The volume percentage of each type is determined by manual measurement of the bands observed under ultra-violet light. The FIA method is time-consuming at ca 4 h per analysis and is highly dependent on interpretation by the analyst. Boundaries are poorly defined, particularly when large amounts of olefins are present. The precision attained is consequently relatively poor.

High Pressure Liquid Chromatography (HPLC) provides a rapid method, which could be automated, to accomplish this analysis with minimum operator attention (2,3,4).

This report describes a method which takes about 20 min per analysis for determining the olefin, saturate and aromatic contents in synthetic fuel naphtha using an HPLC system developed in CANMET's Synthetic Fuels Research Laboratory.

The method meets four basic requirements: rapid determination; reproducible results; minimum exposure of samples to heat, air and light to avoid chemical change; and separated hydrocarbon class concentrates are unaltered chemically.

A model hydrocarbon mixture and three synthetic fuel naphtha fractions were analyzed by this method and some results compared with FIA analyses.

EXPERIMENTAL

A schematic illustrating the processing and separation procedures is shown in Fig. 1.

UPGRADING

The upgraded feeds were heavy oil from the Lloydminster area, bitumen from Cold Lake and a Venezuelan heavy oil (Boscan) which had been vacuum-distilled to remove light ends (5).

DISTILLATION

The processed product was deasphalted and the oil and resin fraction distilled to separate the naphtha fraction up to 200°C under atmospheric pressure.

ANALYZED SAMPLES

Nineteen pure individual hydrocarbons comprising saturates, olefins and monoaromatics as shown in Table 1, and 23 non-hydrotreated naphtha fractions at initial boiling points (IBP) of - 200°C from the processed products of the bitumen and heavy oils, were analyzed.

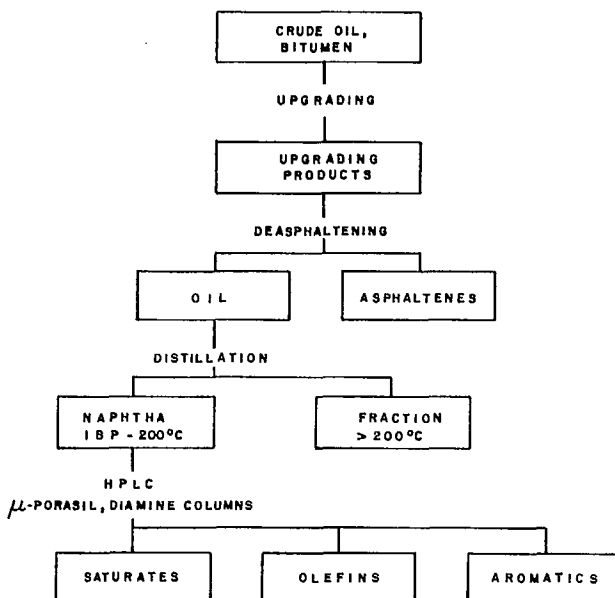


Fig. 1 - Upgrading and separation schematic

Table 1 - High performance liquid chromatographic separation of model hydrocarbon compounds

Compound	Molecular mass	Boiling point (°C)	Peak elution volume (mL)
<u>Saturates</u>			
3-methylhexane	100.20	92	7.76
2,4-dimethylhexane	114.23	110	7.84
2,5-dimethylhexane	114.23	108	7.84
2,3,4-trimethylpentane	114.23	113	7.76
2,2,5-trimethylhexane	114.23	113	7.68
n-nonane	128.25	151	7.82
n-decane	142.28	174	7.84
n-undecane	156.30	196	7.92
<u>Olefins</u>			
hexene-1	84.16	85	8.32
decene-1	140.26	171	8.34
nonene-1	126.24	147	8.37
hexene-2	84.16	85	8.48
2-ethyl hexene-1	112.22	120	8.48
1,3-cyclohexadiene	80.12	81	12.80
2,5-dimethyl-2,4-hexadiene	110.19	103	10.72
<u>Aromatics</u>			
n-butylbenzene	134.21	183	13.65
p-xylene	106.16	138	14.56
toluene	92.13	111	14.10
o-cymene	134.21	176	14.08

COMPOUND-TYPE SEPARATION

A schematic of the apparatus is shown in Fig. 2. The naphtha was separated into compound-type concentrates of saturates, olefins and aromatics using a 10- μ , μ -Bondapak diamine column (25 cm x 4 mm id) coupled to a 10- μ , μ -Porasil (30 cm x 4 mm id) column. A dual-detector system was used consisting of a Waters R401 refractometer for the detection of all compounds and a Schaeffel SF 770 ultraviolet detector for aromatic compounds. The refractometer was temperature-stabilized at 24°C \pm 2°C. Hexane of HPLC grade, dried over activated molecular sieves was used as the mobile phase. The column was reactivated by heating to 120°C for one hour while purging with nitrogen.

RESULTS AND DISCUSSION

The method uses a combination of the HPLC systems developed in the Synthetic Fuels Research Laboratory for separating saturates from aromatics and polar compounds (3) and for separating aromatics into ring classes (6), with the low temperature method developed by Jinno to separate olefins from saturates on silica columns (2). The hydrocarbons are eluted from the activated μ -Porasil and diamine columns with a non-polar mobile phase in an elution-type separation, whereas the FIA method is a displacement-type separation using a polar mobile phase. The order of elution is - saturates, olefins, aromatics. The column is backflushed after the olefins have been eluted

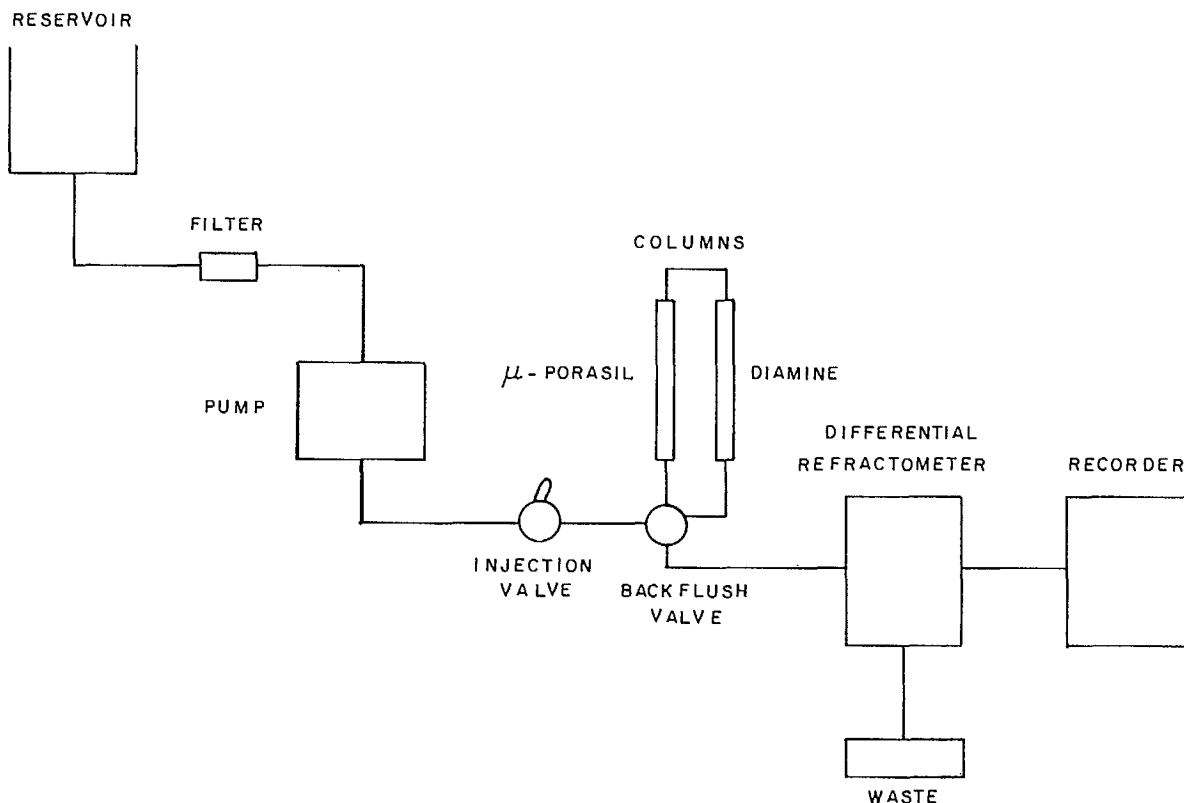


Fig. 2 - Liquid chromatography equipped with backflush

both to ensure that the aromatics elute in a single well-defined peak and to reduce analysis time.

CHROMATOGRAPHY OF THE MODEL HYDROCARBONS

The retention volumes of several saturates, mono-olefins, di-olefins and aromatics were determined (Table 1). The saturates and olefins generally tend to elute in order of increasing carbon number. Lowering the column temperature to 2°C improved resolution and made baseline separation of saturates and olefins possible (Fig. 3). There was also some separation of the mono- and di-olefins. These features are superior to other separations reported in the literature (4,7,8).

CALCULATION OF HYDROCARBON-TYPE CONTENT

The calculations for the hydrocarbon-

types are based on the assumption that all the sample elutes from the column. However, if there is any concentration of polar material in the sample, it is expected to be negligible and will be included in the calculation of the other hydrocarbon groups. Any cyclodi-olefins and thiophenes, if present, will be included with the aromatics.

Because refractive indices vary with the structure and molecular mass of individual hydrocarbons, a blend of compounds corresponding to each hydrocarbon-type was used to establish response factors.

The volume per cent was determined as follows:

$$\% \text{ hydrocarbon type} = \frac{\text{area (hydrocarbon type)} \times \text{response factor}}{[\text{area (saturates + olefins + aromatics)} \times \text{response factors}]} \times 100.$$

Table 2 shows the precision obtained on a standard mixture. The accuracy and precision would be greatly improved if a computing integration could be used to measure peak areas.

CHROMATOGRAPHY OF SYNTHETIC FUEL NAPHTHAS

Representative chromatograms of Lloydminster, Cold Lake and Boscan synthetic naphthas are shown in Fig. 4, 5 and 6. The hydrocarbon type distribution as determined by this method for several naphthas produced under varying pro-

cessing conditions is shown in Tables 3, 4 and 5.

Comparison with the FIA method shows that the standard method gives erroneous low olefinic contents that contribute mainly to the high aromatic content and to a lesser degree to the results obtained for the saturates (Table 3). This makes the HPLC separation superior to the FIA separation method for analyzing synthetic fuel light products containing high percentages of olefinic hydrocarbons.

Table 2 - HPLC analysis of hydrocarbon standard mixture for saturates, olefins and aromatics (30:20:50)

Charge volume, (mL)	Vol %		
	Saturates	Olefins	Aromatics
2.5	31.2	19.5	49.2
2.5	31.4	19.8	48.3
3.0	30.2	20.1	49.4
3.0	31.1	20.5	48.3
4.0	30.8	19.6	49.4
4.0	30.6	19.8	49.3
5.0	30.7	20.6	48.5
5.0	31.8	20.4	47.8
Std dev	0.46	0.40	0.34

Table 3 - Hydrocarbon-type analysis of naphtha from Lloydminster processing products (comparison of FIA and HPLC methods)

Sample	HPLC			FIA		
	Saturates	Olefins	Aromatics	Saturates	Olefins	Aromatics
<u>Lloydminster</u>						
1 (feed)	34.20	25.79	40.00	38.3	10.0	51.7
2	41.13	24.80	34.07	43.5	11.1	45.4
3	37.34	27.43	35.23	42.2	10.9	46.9
4	39.41	27.78	32.81	39.7	10.8	49.5
5	42.37	31.44	26.19	42.7	8.3	49.0
6	43.63	29.20	27.18	44.4	11.5	44.1
7	40.61	28.51	30.88	39.5	11.3	49.2
8	42.72	30.83	26.45	46.9	9.3	43.8

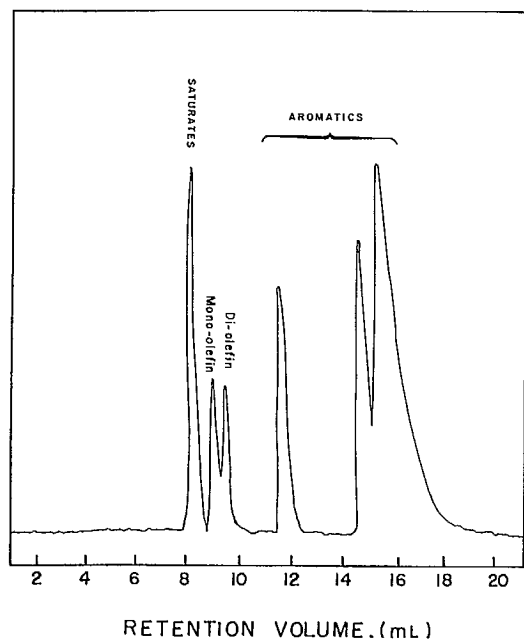


Fig. 3 - Chromatogram of standard sample mixture

Flow rate: 2 mL min⁻¹
 Temperature: 2°C
 Sample size: 2.5 µl
 Sample: Table 1

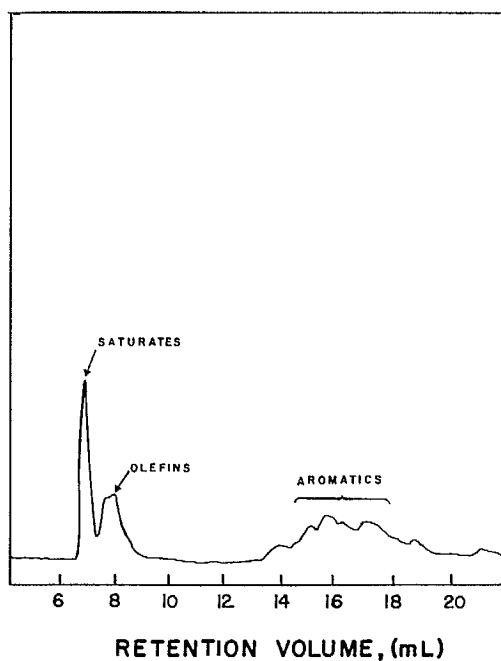


Fig. 4 - Chromatogram of naphtha from Lloydminster hydrocracked product:

Flow rate: 2 mL min⁻¹
 Sample size: 2.5 µl
 Temperature: 2°C

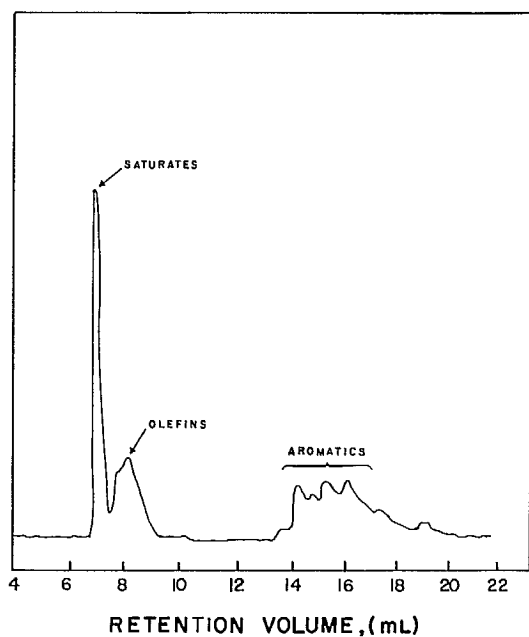


Fig. 5 - Chromatogram of naphtha from Cold Lake hydrocracked product:

Flow rate: 2 mL min⁻¹
 Sample size: 2.5 µl
 Temperature: 2°C

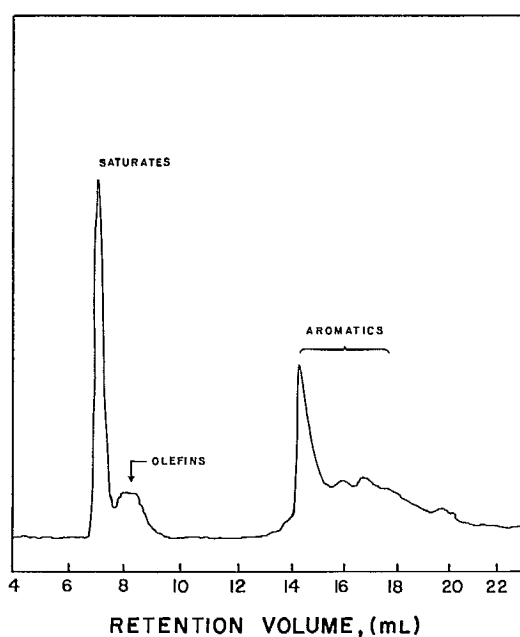


Fig. 6 - Chromatogram of naphtha from Boscan hydrocracked product:

Flow rate: 2 mL min⁻¹
 Sample size: 2.5 µl
 Temperature: 2°C

Table 4 - Hydrocarbon-type analysis of naphtha from Cold Lake processing products using HPLC separation

Sample	1	2	3	4	5	6	7	8	9	10
Compound-type (vol %)										
Saturates	57.23	59.91	65.74	63.22	67.76	57.23	61.0	52.23	58.60	51.50
Olefins	30.56	31.75	17.46	23.32	19.87	32.54	30.52	31.50	29.20	36.46
Aromatics	12.21	9.02	16.74	12.43	12.36	9.16	8.46	16.27	12.18	12.04

Table 5 - Hydrocarbon-type analysis of naphtha from Boscan processing products using HPLC separation

Sample	1	2	3	4	5
Compound-type (vol %)					
Saturates	60.86	62.51	63.68	64.47	66.25
Olefins	17.78	20.32	22.09	23.04	23.42
Aromatics	21.35	17.38	14.21	12.46	10.31

CONCLUSION

An HPLC method was developed for analyzing petroleum and synthetic fuel light products with high olefinic content. The method provides shorter analysis time, less operator involvement and results that are independent of analyst interpretation. The method is also capable of being automated with the results being reported in the form of a printout at the end of the analysis.

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