GAS CHROMATOGRAPHIC SEPARATION, BY CARBON NUMBER AND HYDROCARBON TYPE, OF SATURATED HYDROCARBON MIXTURES AND DIFFERENT NAPHTHAS OVER MOLECULAR SIEVES 13X

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SUMMARY

A gas–solid chromatographic method is described for separating hydrocarbon mixtures according to hydrocarbon type and carbon number by the use of molecular sieves 13X.

Practical applications of this analytical method are reported, including the analysis of the charge and the end-products of a platforming plant, and in addition, some quantitative and qualitative determinations on virgin naphtha from different types of crude oil.

INTRODUCTION

This paper proposes an extension of the method described by BRUNNOCK AND LUN for the rapid separation of the hydrocarbons, according to carbon number, in saturated petroleum distillates up to 185 . This procedure permits the separation and determination of naphthenes, *iso*-paraffins, *n*-paraffins and results in improved accuracy for the evaluation of straight-run naphthas. Because the aromatic hydrocarbons are partially and irreversibly adsorbed by molecular sieves, they must be separately determined according to the ASTM D-2267 method.

The object of this analytical investigation was to identify the various components of virgin naphtha and to relate them to the yield of effluent products in the refinery operations.

The methods commonly used to determinate total *iso*- and *n*-paraffins (P), olefins (O), naphthenes (N) and aromatics (A) content are usually P.O.N.A. method (UOP Method 273-64), or more sophisticated techniques such as capillary column chromatography and mass spectrometry. These methods give a series of data that are useful in research, but the long operating time required makes routine application difficult.

The procedure described in this paper for the determination of hydrocarbons by types and by the number of carbon atoms, is simple as well as a valid alternative to the methods mentioned above.

EXPERIMENTAL AND RESULTS

The apparatus and experimental conditions were as follows. The gas chromatograph was a Perkin-Elmer Model F 11 with a flame ionization detector (single flame),

TABLE I

ANALYSIS OF ARTIFICIAL HYDROCARBON MIXTURE NO. 1 (10 RUNS)

Mixture No. 1	Wt.-% expected	Wt.-% found										Average	Average Δ	Δmin.	Δmax.
		1	2	3	4	5	6	7	8	9	10				
n-C$_6$ (n-hexane)	18.93	19.98	19.38	18.23	19.04	19.43	19.23	18.28	19.00	19.12	18.96	19.07	+0.14	−0.70	+1.05
iso-C$_7$ (n-heptane)	19.80	21.00	20.43	19.61	19.91	20.75	20.46	19.63	21.18	20.18	20.27	20.34	+0.54	−0.19	+1.20
n-C$_8$ (n-octane)	19.83	20.75	20.58	20.41	19.74	20.08	20.59	20.86	20.93	20.56	20.34	20.57	+0.74	−0.09	+1.15
n-C$_9$ (n-nonane)	20.23	20.05	20.18	20.88	19.24	20.52	20.44	21.34	20.47	20.07	20.06	20.39	+0.16	−0.99	+1.11
n-C$_{10}$ (n-decane)	21.21	18.22	19.43	20.87	22.07	18.32	19.28	19.86	18.42	19.47	20.37	19.63	−1.58	−2.99	+0.86

TABLE II

ANALYSIS OF ARTIFICIAL HYDROCARBON MIXTURE NO. 2 (4 RUNS)

Mixture No. 2	Wt.-% expected	Wt.-% found				Average	Average Δ	Δmin.	Δmax.
		1	2	3	4				
C$_6$ Naphthenes (cyclohexane)	8.12	8.47	8.21	8.15	7.85	8.17	+0.05	−0.27	+0.35
iso-Paraffins (2,3-dimethylbutane)	7.01	7.12	7.05	7.04	6.97	6.97	+0.04	−0.34	+0.11
n-Paraffins (n-hexane)	0.83	0.87	0.80	0.79	0.35	0.70	+0.13	−0.48	+0.04
C$_7$ Naphthenes (methylcyclohexane)	8.31	8.07	8.12	8.04	8.05	8.07	−0.24	−0.27	−0.19
iso-Paraffins (3-methylhexane)	6.52	6.48	6.51	6.72	6.32	6.51	−0.01	−0.20	+0.20
n-Paraffins (n-heptane)	7.27	7.04	7.23	7.07	7.32	7.17	−0.10	−0.23	+0.05
C$_8$ Naphthenes (1,2-dimethylcyclohexane)	8.50	8.80	8.60	8.68	9.13	8.80	+0.30	+0.10	+0.63
iso-Paraffins (3-methylheptane)	7.47	7.51	7.38	7.47	7.79	7.54	+0.07	−0.09	+0.32
n-Paraffins (n-octane)	7.46	7.51	7.35	7.39	8.23	7.62	+0.16	−0.23	+0.77
C$_9$ Naphthenes (1,3,5-trimethylcyclohexane)	8.45	10.00	9.93	10.07	8.92	9.73	+1.28	+0.47	+1.62
iso-Paraffins (4-methyloctane)	8.01	7.95	8.02	8.27	8.28	8.13	+0.12	−0.06	+0.27
n-Paraffins (n-nonane)	8.03	7.39	7.86	7.66	8.28	7.80	−0.23	−0.37	+0.17
C$_{10}$ n-Paraffins (n-decane)	8.01	0.78	0.94	6.64	6.81	0.79	−1.22	−1.37	−1.07

connected to a Hitachi Perkin-Elmer Model 159 recorder with a 1 mV range and a chart speed of 5 mm/min.

Fig. 1. Schematic diagram of chromatographic column.

The chromatographic column was of length 90 cm and I.D. 1/16 in., made of annealed steel and filled as shown in Fig. 1. The components shown in Fig. 1 are the following. E is the carrier gas input, o is the carrier gas output, a is 1 in. of quartz wool, b is 1½ in. of Chromosorb P, 30–60 mesh, c is molecular sieves 13X, 30–60 mesh (from Curtin, Linde, Union Carbide, U.S.A.), and d is 1 in. of quartz wool. The molecular sieves (30–60 mesh) were treated with NaOH (3% aqueous solution), rinsed with water to neutrality and dried in an oven at 100 for 24 h. Subsequently the sieves were kept in an oven at 200 for 24 h and then sieved.

The initial temperature was 180, and the temperature programming consisted

TABLE III

ANALYSIS OF ARTIFICIAL HYDROCARBON MIXTURES NO. 3 AND 4, EACH WITH AND WITHOUT XYLENES (4 RUNS)

The adsorption of xylenes is evident (> 50%); the adsorption is less for toluene. The results for the mixtures with and without xylenes confirm the marked adsorption of xylenes.

Mixture	Wt.-% expected	Wt.-% found				Average	Average Δ	Δmin.	Δmax.
		1	2	3	4				
Mixture No. 3, with xylenes									
n-Hexane	31.83	34.67	35.27	34.30	34.15	34.60	+2.77	+2.32	+3.44
n-Heptane	31.86	35.09	34.72	34.52	34.28	34.65	+2.79	+2.42	+3.23
Benzene	12.13	13.54	13.33	13.32	12.90	13.27	+1.04	+0.77	+1.41
Toluene	12.26	11.78	11.60	11.57	11.71	11.67	−0.59	−0.69	−0.48
Xylenes	11.92	4.92	5.08	6.29	6.96	5.81	−6.11	−7.00	−4.96
Mixture No. 3, without xylenes									
n-Hexane	36.14	36.46	37.16	36.60	36.70	36.73	+0.59	+0.32	+1.02
n-Heptane	36.17	36.91	36.58	36.84	36.84	36.79	+0.62	+0.41	+0.14
Benzene	13.77	14.24	14.04	14.21	13.87	14.09	+0.32	+0.10	+0.47
Toluene	13.92	12.39	12.22	12.35	12.59	12.39	−1.53	−1.70	−1.33
Xylenes	—	—	—	—	—	—	—	—	—
Mixture No. 4, with xylenes									
n-Hexane	16.61	18.70	18.82	18.92	20.09	19.13	+2.52	+2.09	+3.48
n-Heptane	17.15	19.09	18.99	19.14	20.05	19.32	+2.17	+1.84	+2.90
Benzene	22.26	25.10	24.68	24.65	25.27	24.93	+2.77	+2.39	+3.01
Toluene	21.73	22.10	22.24	22.31	23.28	22.48	+0.75	+1.37	+1.55
Xylenes	22.25	15.01	15.27	14.98	11.31	14.14	−8.11	−10.94	−6.98
Mixture No. 4, without xylenes									
n-Hexane	21.36	22.00	22.21	22.26	22.65	22.28	+0.92	+0.64	+1.29
n-Heptane	22.06	22.46	22.42	22.51	22.01	22.50	+0.44	+0.36	+0.55
Benzene	28.63	29.53	29.12	28.99	28.49	29.03	+0.40	−0.14	+0.90
Toluene	27.95	26.01	26.25	26.24	26.25	26.19	−1.76	−1.94	−1.70
Xylenes	—	—	—	—	—	—	—	—	—

TABLE IV

RESULTS FOR OCCIDENTAL VIRGIN NAPHTHA

In Tables IV to VIII: aromatics were determined by the ASTM D-2267 method and the results in % by volume are transformed into % by weight; the values obtained from the analysis on molecular sieves (M.S.) 13X and on a capillary column (C.C.) are expressed in % by weight; C_4 includes iso- and n-butane.

Density, 15/4 = 0.7159 (API 66.1).

	Vol.-% recovered	B.p. (°C)
ASTM D-86:	initial	48
	5	68
	10	74
	30	88
	50	101
	70	116
	90	134
	95	142
	Final	149

Analysis (Vol.-%): P = 69.5; O = 0.2; N = 25.6; A = 4.7.

Carbon number	Naphthenes		iso-Paraffins		n-Paraffins		Aromatics
	C.C.	M.S. 13X	C.C.	M.S. 13X	C.C.	M.S. 13X	
C_4			0.19	0.16[b]	0.96	0.65[b]	
C_5	0.62	0.65	4.12	4.15	5.50	5.49	
C_6	5.02	5.61	7.63	8.34	6.89	7.19	0.45
C_7	10.54	11.26	7.36	7.98	7.05	7.82	2.12
C_8	8.72	8.69	7.91	7.93	6.47	6.11	3.16
C_9	3.59	3.99	5.61	5.09	3.25	2.19	0.80
C_{10}	0.23		1.03	0.17	0.20		
Total	28.72	30.20	33.82	33.82	30.02	29.45	6.53

TABLE V

RESULTS FOR MIDDLE EAST VIRGIN NAPHTHA

For explanation, see Table IV.

Density, 15/4 = 0.7219 (API 64.5).

	Vol.-% recovered	B.p. (°C)
ASTM D-86:	Initial	54
	5	77
	10	83
	30	100
	50	113
	70	126
	90	143
	95	152
	Final	164

Analysis (vol.-%): P = 73.6; O = 0.2; N = 18.4; A = 7.8.

Carbon number	Naphthenes		iso-Paraffins		n-Paraffins		Aromatics
	C.C.	M.S. 13X	C.C.	M.S. 13X	C.C.	M.S. 13X	
C_4			0.11	0.11	0.91	0.85	
C_5	0.33	0.41	1.87	2.21	3.79	4.20	
C_6	2.90	3.34	5.76	6.66	7.17	7.76	0.48
C_7	5.32	5.72	7.41	8.05	9.42	9.64	2.59
C_8	5.81	5.66	9.99	10.27	9.40	8.97	5.04
C_9	4.03	3.70	6.95	7.62	4.76	3.74	1.86
C_{10}	0.23	0.10	2.94	0.93	0.90	0.15	
Total	18.62	18.93	35.03	35.79	36.35	35.31	9.97

TABLE VI

RESULTS FOR SASSAN RAS TANURA VIRGIN NAPHTHA

For explanation, see Table IV.
Density, $15/4° = 0.7194$ (API 65.1).

	Vol.-% recovered	B.p. (°C)
ASTM D-86:	Initial	53
	5	78
	10	84
	30	98
	50	110
	70	123
	90	140
	95	146
	Final	150

Analysis (vol.-%): $P = 74.62$; $O = 0.37$; $N = 16.46$; $A = 8.55$.

Carbon number	Naphthenes		iso-Paraffins		n-Paraffins		Aromatics
	C.C.	M.S. 13X	C.C.	M.S. 13X	C.C.	M.S. 13X	
C$_4$					1.18	1.41	
C$_5$	0.10	0.27	1.63	2.40	2.72	3.70	
C$_6$	3.94	4.20	4.28	5.35	7.33	8.81	0.61
C$_7$	5.46	6.22	7.72	9.23	10.33	11.08	3.81
C$_8$	5.96	5.11	9.45	9.53	9.11	8.24	5.62
C$_9$	2.83	3.22	8.00	6.58	5.85	3.37	1.23
C$_{10}$	0.27		2.60		0.34		
Total	18.26	19.02	33.68	33.09	39.76	36.61	11.27

TABLE VII

RESULTS FOR SARIR VIRGIN NAPHTHA

For explanation, see Table IV.
Density, $15/4° = 0.719$ (API 65.2).

	Vol.-% recovered	B.p. (°C)
ASTM D-86:	Initial	45
	5	68
	10	74
	30	91
	50	104
	70	115
	90	130
	95	137
	Final	147

Analysis (vol.-%): $P = 64.88$; $O = 0.20$; $N = 32.22$; $A = 2.70$.

Carbon number	Naphthenes		iso-Paraffins		n-Paraffins		Aromatics
	C.C.	M.S. 13X	C.C.	M.S. 13X	C.C	M.S. 13X	
C$_4$					1.32	1.22	
C$_5$	0.74	0.62	3.78	4.38	5.58	5.93	
C$_6$	5.11	5.80	5.26	6.13	6.93	7.08	0.55
C$_7$	11.74	12.55	5.80	6.34	8.44	8.29	1.17
C$_8$	12.96	12.67	8.33	7.71	9.24	8.18	2.16
C$_9$	3.69	4.42	4.72	3.48	2.10	1.05	0.09
C$_{10}$	0.05	—	0.21	0.18	0.02	—	—
Total	34.29	36.06	28.10	28.22	33.63	31.75	3.97

TABLE VIII

PLATFORMING: ANALYSIS OF FEED AND EFFLUENTS FROM REACTORS R_2, R_3 AND R_1 (LIQUID PHASE ONLY)

For explanation, see Table IV.

Carbon number	Feed				Output R_2				Output R_3				Output R_1			
	Naph.	iso-P.	n-P.	Arom.	Naph.	iso-P.	n-P.	Arom.	Naph.	iso-P.	n-P.	Arom.	Naph.	iso-P.	n-P.	Arom.
C_2							0.19				0.18				0.14	
C_3							1.12				1.17				1.20	
C_4						1.28	1.43			1.50	1.85			1.78	2.41	
C_5	0.07				0.10	1.09	1.03		0.13	3.04	1.07		0.10	4.72	2.93	
C_6	7.31	0.03	0.04	0.62	4.74	8.53	8.12	2.09	1.93	11.54	7.12	3.29	0.09	13.42	6.11	6.05
C_7	15.41	5.08	8.74	2.42	5.21	12.07	7.94	10.48	0.77	13.84	5.16	15.06	0.48	10.36	2.80	19.26
C_8	12.03	10.50	10.34	3.34	1.98	9.76	3.97	12.07	0.25	8.05	1.97	16.41	0.18	3.31	0.61	19.88
C_9	3.02	0.88	7.29	0.10	0.43	1.85	0.09	2.10	0.21	0.98	0.11	3.17	0.00	0.09		3.36
C_{10}		2.86	0.23													
Total	37.84	29.04	26.04	6.48	12.46	36.29	23.01	27.34	3.29	38.95	19.23	38.53	1.57	33.68	16.20	48.55

of sampling to 330° at 5°/min, then from 330° to 450° at 2°/min. The evaporator temperature was 200°.

The carrier gas was helium at an inlet pressure of 1.2 kg/cm², splitter 300 ml/min.

A series of artificial hydrocarbon mixtures was prepared and analyzed by the present method to check for eventual irreversible adsorption of heavy compounds and to lay the basis for quantitative analysis. The results are shown in Tables I, II and III.

It can be seen that, with the exception of the aromatics, the other hydrocarbons have a response coefficient to each other which can be considered to be unity in all instances. For the aromatics, the following correction factors, F, were found experimentally: n-heptane, 1.000; benzene, 0.8929; toluene, 0.9345; and xylenes, 0.9780.

As shown in Tables I, II and III, by applying the correction factors relative to these components in the flame ionization detection, a good correlation is seen between the expected values and those found experimentally, although some adsorption of toluene and n-decane is observed. The results for xylenes and heavier aromatics obtained by this method are unreliable. Therefore, this method is applicable only to saturated hydrocarbons up to n-decane. Other methods (e.g., ASTM D-2267) must be used for the determination of the aromatics.

Subsequently, actual samples of virgin naphtha from various crude oils (Occidental, Middle East, Sassan and Sarir) were analyzed. The separation by carbon number and hydrocarbon type was accomplished by using molecular sieves 13X and the chromatogram is shown in Fig. 2. The samples were also analyzed by P.O.N.A. (UOP Method 273-64) and capillary column (C.C.) chromatography according to the method described by LEVEQUE[2].

The results are given in Tables IV to VII. It should be noted that values obtained by molecular sieves and capillary columns are expressed in % by weight, while values obtained by P.O.N.A. method are in % by volume.

The molecular sieve method was also applied to characterize the feed and the effluent products, at various stages of reaction (liquid phase only), of a platforming plant (Table VIII and Fig. 3).
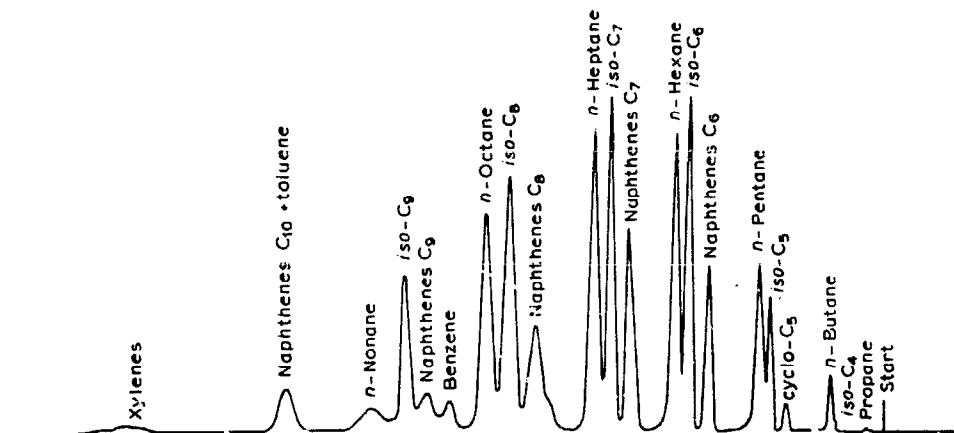

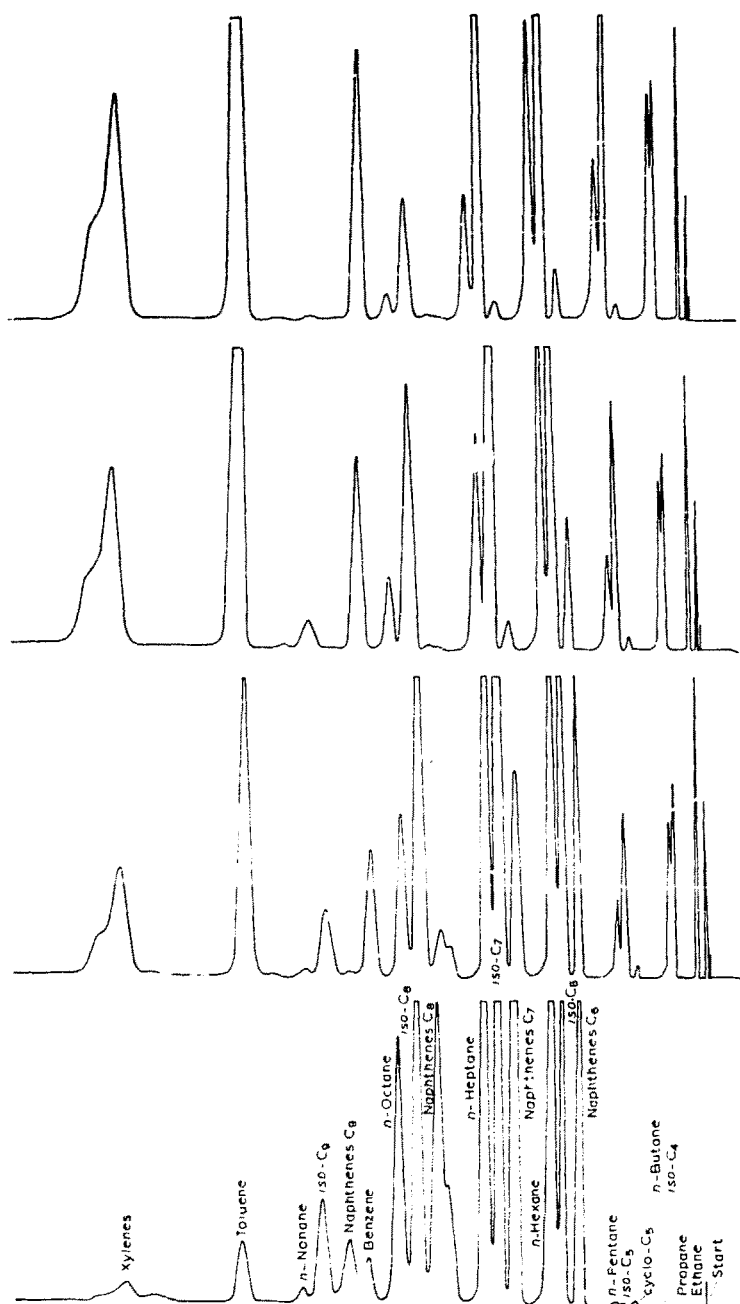Fig. 2. Gas chromatogram of Occidental virgin naphtha.

Fig. 3. Four chromatograms of, from the bottom to the top, the stream from the reactor in the platforming plant, and the streams from the first, second and third platforming reactor

REFERENCES

1 J. V. BRUNNOCK AND L. A. LUKE, *Anal. Chem.*, 40 (1968) 2158.
2 R. E. LEVEQUE, *Anal. Chem.*, 39 (1967) 1811.