

REFINERY	PETROL
OLEFINES	PROPORTIONS
HEXENES	HEPTENES
ISOMERS	SEPARATION
ANALYSIS	GC-MS

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Characterization of sixty alkenes in a cat-cracked gasoline naphtha by gas chromatography

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**Characterization of Sixty Alkenes in a
Cat-cracked Gasoline Naphtha by
Gas Chromatography**

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Key Words

Gas chromatography – mass spectrometry

Light FCC naphtha

C₅-C₇ Alkene composition

Alkene retention data

Summary

The alkene-rich petrol fraction from refinery fluid catalytic cracking (FCC) has been characterized by GC and GC-MS. Quantitative proportions and retention data of 52 acyclic and 11 cyclic C₅-C₇ alkenes are given. Relative retentions are reported for methylsilicone and aluminium oxide stationary phases as methylene units (MU). Applications of mass spectra, single-ion GC-MS monitoring and retention data for identifications are demonstrated.

Introduction

Alkenes give rise to photooxidants in rapid atmospheric reactions which differ considerably even between different isomers [1]. Major anthropogenic emissions of volatile alkenes are due to petrol-fuelled vehicles [2]. Speciated determinations of alkenes are therefore of interest not only in air pollution studies but also in refinery, fuel and motor technology [3, 4].

In contrast to the combustion-formed short-chain alkenes, the C₅-C₇ alkenes in exhaust emissions from vehicles are mainly unburnt fuel components [2]. They originate predominantly from the light FCC naphtha fraction of the petrol [3]. Most studies of alkenes in fuels [3], emissions [2], and urban air [5] have been limited to C₅ and lower alkenes, because of the large number and isomeric complexity of C₆ and higher alkenes. In previous reports, the pentenes [6] and the 17 isomeric acyclic hexenes [7] were studied in petrol vapour. The analysis of a FCC naphtha permits the acquisition of more comprehensive alkene data of chromatographic, environmental as well as technical relevance.

Experimental

Light FCC naphtha, produced from desulphurized vacuum gas oil, was obtained from the Scanraff refinery in Lysekil, Sweden. The naphtha contained hydrocarbons in the boiling point range 20-140 °C. At the refinery it is used as a major component in the production of commercial petrol.

The methylsilicone GC data refer to a DB-1 stationary phase on a 50 m x 0.32 mm i.d. fused silica open tubular column (J&W) with a thick (1 µm) phase layer. The linear temperature increase was 2 °C min⁻¹ from -20 °C. The aluminium oxide GC

data were obtained for an $\text{Al}_2\text{O}_3/5\%$ KCl phase on a 50 m x 0.32 mm i.d. fused silica PLOT column (Chrompack). The linear temperature increase was $2\text{ }^\circ\text{C min}^{-1}$ from $100\text{ }^\circ\text{C}$ after a rapid initial temperature increase. Helium was used as carrier gas with a linear gas velocity of the order of 20 cm s^{-1} .

The FCC naphtha was analysed as both liquid samples and as gaseous samples taken with a syringe above the liquid phase. Adsorbent sampling in a vessel with completely evaporated naphtha, followed by thermal desorption and gas chromatography, was also used to obtain data for the alumina column. Similar techniques were previously used for the analysis of petrol vapour hydrocarbons [6] including hexenes [7], on the same column but with different temperature programs. Quantitative GC data were obtained with flame ionization detection without corrections for response differences between the hydrocarbons.

The mass spectrometer was a Varian Saturn II ion trap GC-MS instrument. The columns and the chromatographic data were similar and comparable for the GC and the GC-MS studies of the naphtha. The scan range was m/z 35-200 and the scan frequency was one scan per second. Reconstructed mass spectra and ion chromatograms were obtained from the data-stored

scans. Reference spectra of most of the C₅-C₇ alkenes were available for comparison from the data-stored library (NIST) of mass spectra.

Results and discussion

Alkenes in the FCC naphtha

In Table I, the hydrocarbon composition is given for the light FCC naphtha studied. The results were obtained from GC analysis. It is seen that the total proportion of acyclic and cyclic alkenes was just over 40 %. A control sample obtained one year later contained somewhat smaller amounts of alkenes and significantly smaller amounts of cycloalkenes and alkadienes. The proportions of different hydrocarbon classes are known to depend on operational parameters and may differ considerably, particularly between different refineries [3]. The proportions between isomers are more uniform, as previously discussed for hexenes [7].

In Table II, results are given for all pentenes and hexenes, and for all heptenes constituting more than 0.1% of the total C₅-C₇ alkenes. All acyclic C₅-C₇ alkenes are within the boiling point range 20-100 °C. As expected, the proportions in the gas phase differ from those in the liquid phase according to volatility as reflected by the boiling points. Unbranched isomers and

isomers which are methyl-branched at the double bond predominate among the non-cyclic alkenes. The most prominent single isomers are the 2-methyl-2-alkenes. Among the C₆-C₇ cycloalkenes, the most prominent isomers are branched at the double bond.

Retention data

Relative retentions for linear temperature-programmed analysis are given in Table II as methylene units (MU), corresponding to the retention index defined for isothermal analysis. Relative retentions depend to some extent on temperature, and consequently MU values depend on the temperature program. A linear temperature increase starting from a low temperature was chosen for both the methylsilicone and the alumina columns to give MU values of wide applicability. As a result, the MU difference between an alkene and the next higher homologous alkene is near to 1.0 which may facilitate and confirm identifications.

The alkene isomers in Table II have been ordered according to increasing retention on the methylsilicone column. The retention order of the isomers closely follows the order of increasing boiling points. The *trans* isomers which are unbranched at the olefinic (α) carbon atoms are somewhat less retained than their boiling points might suggest.

On the methylsilicone column, the alkenes appear in the same MU range as the corresponding alkanes, although the dependence of retention order on isomer structure is different. Not only unbranched but also α -branched alkene isomers appear later than other branched alkene isomers. Branching at non-olefinic carbon atoms decreases retention as with alkanes, and β -branching causes a specific further decrease. The 1-alkene isomers appear before the corresponding 2- and 3-alkenes. The reported MU values compare well with published retention index data for several alkenes [8, 9] on methylsilicone phases.

On the polar alumina column, the alkenes are retained more strongly than the corresponding alkanes. On the other hand, the MU range for each group of alkene isomers is smaller than for the methylsilicone. Several retention characteristics can be ascribed to steric hindrance of interactions between the double bond of the alkenes and the polar stationary phase. Branching at an olefinic carbon atom decreases retention, particularly for internal alkenes. The *trans* isomers which are unbranched at the olefinic carbon atoms appear before (~ 0.2 MU) the *cis* isomers. The 1-alkenes are rather more strongly retained than the corresponding 2- and 3-alkenes. These MU shifts cause the retention order of isomeric alkenes to be quite different from that on the methylsilicone phase. The effects of branching at the

non-olefinic carbon atoms are similar for both stationary phases, however.

Gas chromatography and mass spectrometry

The chromatograms given in Figure 1 illustrate the usefulness of GC-MS for the separation and identification of alkenes in FCC naphtha. Hexanes and hexenes appear in the same chromatographic range on the non-polar column. The m/z 67 ion chromatogram specifically records the three methylcyclopentenes, although they are all unresolved from other prominent hydrocarbons. The co-elution of 1-methylcyclopentene with benzene on methylsilicone columns may easily be overlooked, although this danger has been emphasized for standardized determinations of benzene [10]. A previous comparable GC-MS study of hexenes demonstrates the performance of the alumina column [7].

For structural identifications, the mass spectra of the reported C_5 - C_7 alkenes were compared with reference spectra and interpreted with respect to mass spectrometric fragmentation. Observed peaks considered to be of particular value for structural assignments are indicated in Table II by their m/z values. Most of the alkenes exhibit characteristic peaks at even mass numbers from their molecular ions. Many isomers give rise to abundant odd-mass ions by allylic cleavage of the

molecular ion with loss of an alkyl radical. Hydrogen rearrangements with loss of an alkene moiety result in specific even-mass peaks, particularly for several 1-alkenes. In spite of these specific fragmentations, the mass spectra of several isomers are very similar, and retention data from the two GC columns were needed for final structural assignments.

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Table I The FCC naphtha characterized by its composition (% w/w) of hydrocarbon categories*.

	Total	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉
Alkanes	29.6	0.1	9.6	8.8	5.6	3.5	2.0
Alkenes	31.7	0.6	13.6	10.4	5.8	1.3	–
Alkadienes	0.7	–	0.3	0.4	–	–	–
Cycloalkanes	9.2	–	0.2	2.8	3.7	2.5	–
Cycloalkenes	6.8	–	0.7	2.2	2.4	1.5	–
Cycloalkadienes	0.3	–	0.1	0.2	–	–	–
Arenes	14.7	–	–	1.0	4.3	6.7	2.7

*The results were obtained by appropriate summing of 120 identified hydrocarbons (89% of the naphtha) and additional compounds (4% of the naphtha) identified only as to structural class. The remaining portion of the naphtha consists mainly of about 1% each of C₈-C₁₀ alkanes, C₈-C₉ alkenes, C₇-C₉ alkadienes, C₈-C₉ cycloalkanes, C₈-C₉ cycloalkenes and C₉-C₁₀ arenes.

Table II. Analytical data for C₅-C₇ alkenes in the FCC naphtha.*

Alkenes	Relative proportions		Boiling point °C	Relative retentions		Specific MS ions <i>m/z</i>
	Liquid %	Gas %		Methylsilicone MU	Al ₂ O ₃ /KCl MU	
C5 Acyclic	39.0	71.1				
3-Methyl-1-butene	0.8	2.9	20.1	4.50	5.24	70,55
1-Pentene	3.7	8.6	30.0	4.86	5.41	70,42
2-Methyl-1-butene	6.5	14.4	31.2	4.95	5.43	70,55
<i>E</i> -2-Pentene	9.9	16.4	36.4	5.08	5.29	70,55
<i>Z</i> -2-Pentene	5.4	9.4	36.9	5.15	5.50	70,55
2-Methyl-2-butene	12.7	19.4	38.5	5.19	5.38	70,55
C6 Acyclic	29.6	17.6				
3,3-Dimethyl-1-butene	0.1	0.1	41.2	5.12	6.05	84,69
4-Methyl-1-pentene	0.6	0.5	53.9	5.54	6.29	84,43
3-Methyl-1-pentene	0.8	0.6	54.2	5.55	6.19	84,69
2,3-Dimethyl-1-butene	0.7	0.6	55.6	5.64	6.23	84,69
<i>Z</i> -4-Methyl-2-pentene	0.5	0.4	56.4	5.66	6.20	84,69
<i>E</i> -4-Methyl-2-pentene	1.5	1.1	58.6	5.69	6.05	84,69
2-Methyl-1-pentene	2.6	1.7	62.1	5.87	6.42	84,56
1-Hexene	1.5	0.9	63.5	5.88	6.45	84,56
2-Ethyl-1-butene	0.9	0.5	64.7	5.99	6.39	84,69
<i>E</i> -3-Hexene	1.9	1.2	67.1	6.02	6.23	84,55
<i>Z</i> -3-Hexene	0.8	0.5	66.4	6.03	6.43	84,55
<i>E</i> -2-Hexene	4.0	2.2	67.9	6.05	6.30	84,55
2-Methyl-2-pentene	4.3	2.5	67.3	6.07	6.25	84,69
<i>Z</i> -3-Methyl-2-pentene	2.5	1.4	67.7	6.10	6.28	84,69
<i>Z</i> -2-Hexene	2.2	1.2	68.9	6.14	6.50	84,55
<i>E</i> -3-Methyl-2-pentene	3.8	1.8	70.4	6.20	6.29	84,69
2,3-Dimethyl-2-butene	0.9	0.4	73.2	6.30	6.23	84,69
C7 Acyclic	16.4	5.0				
2,4-Dimethyl-1-pentene	0.2	0.1	81.6	6.46	7.14*	56
3-Methyl-1-hexene	0.1	0.0	83.9	6.50	7.20	70,69
2-Ethyl-3-methyl-1-butene	0.1	0.0	86.4	6.52	7.14*	98,83
2,4-Dimethyl-2-pentene	0.3	0.1	83.3	6.55	6.97	98,83
5-Methyl-1-hexene	0.1	0.0	85.3	6.57	7.35	56
2,3-Dimethyl-1-pentene	0.3	0.1	84.3	6.58	7.14	98,69
<i>E</i> -2-Methyl-3-hexene	0.5	0.2	85.9	6.61	6.95	98,69
4-Methyl-1-hexene	0.1	0.0	86.7	6.64	7.28	57,56
<i>E</i> -4-Methyl-2-hexene	0.6	0.2	87.6	6.66	6.92	98,69
<i>Z</i> -4-Methyl-2-hexene	0.3	0.1	86.3	6.66	7.13	98,69
<i>Z</i> -2-Methyl-3-hexene	0.2*	0.1	86.1	6.67	7.12	98,69
<i>E</i> -5-Methyl-2-hexene	0.6*	0.2	88.1	6.69	7.15	98,56
<i>Z</i> -3,4-Dimethyl-2-pentene	0.2	0.1	89.3	6.79	7.11	98,83
<i>Z</i> -5-Methyl-2-hexene	0.3	0.1	89.5	6.80	7.36	98,56
2-Methyl-1-hexene	0.9	0.3	92.0	6.86	7.42	56
<i>E</i> -3,4-Dimethyl-2-pentene	0.5*	0.2	91.5	6.88	7.11	98,83
1-Heptene	0.5	0.2	93.6	6.89	7.48	56,70
2-Ethyl-1-pentene	0.5	0.2	94.0	6.90	7.34	98,70
<i>E</i> -3-Methyl-3-hexene	0.4*	0.1	93.5	6.95	7.21	98,69
<i>Z</i> -3-Methyl-3-hexene	0.3*	0.1	95.4	6.95	7.21	98,69
<i>E</i> -3-Heptene	1.6	0.5	95.7	6.98	7.24	98,56
<i>Z</i> -3-Heptene	0.8	0.2	95.8	7.01	7.45	98,56
2-Methyl-2-hexene	1.9	0.5	95.4	7.02	7.23	98,69
<i>Z</i> -3-Methyl-2-hexene	0.9	0.3	97.3	7.03	7.25	98,69
<i>E</i> -2-Heptene	1.3	0.4	97.9	7.05	7.30	98,56
3-Ethyl-2-pentene	0.4	0.1	96.0	7.07	7.25*	98,69
<i>E</i> -3-Methyl-2-hexene	1.2	0.3	95.2	7.09	7.25	98,69
<i>Z</i> -2-Heptene	0.8	0.2	98.4	7.12	7.51	98,56
2,3-Dimethyl-2-pentene	0.5	0.1	97.4	7.13	7.11	98,83

Alkenes	Relative proportions		Boiling point °C	Relative retentions		Specific MS ions <i>m/z</i>
	Liquid %	Gas %		Methylsilicone MU	Al ₂ O ₃ /KCl MU	
Cycloalkenes	14.7	6.1				
C5						
Cyclopentene	2.1	2.2	44.2	5.48	5.26	68,67
C6						
3-Methylcyclopentene	1.0	0.5	64.9	6.08	6.13*	82,67
4-Methylcyclopentene	0.5	0.3	65.7	6.11	6.13*	82,67
1-Methylcyclopentene	4.2	1.6	75.5	6.48	6.13	82,67
Cyclohexene	0.6	0.2	83.0	6.73	6.39	82,54
C7						
1,3-Dimethylcyclopentene	1.2	0.2	92	6.98	6.86	96,81
1,4-Dimethylcyclopentene	1.0	0.3	93.2	7.00	6.92*	96,81
1,5-Dimethylcyclopentene	0.9	0.2	102	7.06	6.90*	96,81
1,2-Dimethylcyclopentene	2.0	0.4	105.8	7.10	6.86	96,81
1-Ethylcyclopentene	0.5	0.1	106.3	7.52	7.05	96,67
1-Methylcyclohexene	0.7	0.1	110.3	7.67	7.14	96,81

* The composition is given as percent of the sum of the 63 alkenes. Uncertain data are marked by an asterisk. Boiling point data are given according to the TRC (Thermodynamics Center, Texas) Thermodynamic Tables. Additional dimethylcyclopentene isomers sum up to 0.5 %. The two most prominent C₈ alkenes were found to be 1,2,3-trimethylcyclopentene and 1,2,4-trimethylcyclopentene, each amounting to 1 % of total C₅-C₇ alkenes in the liquid phase.

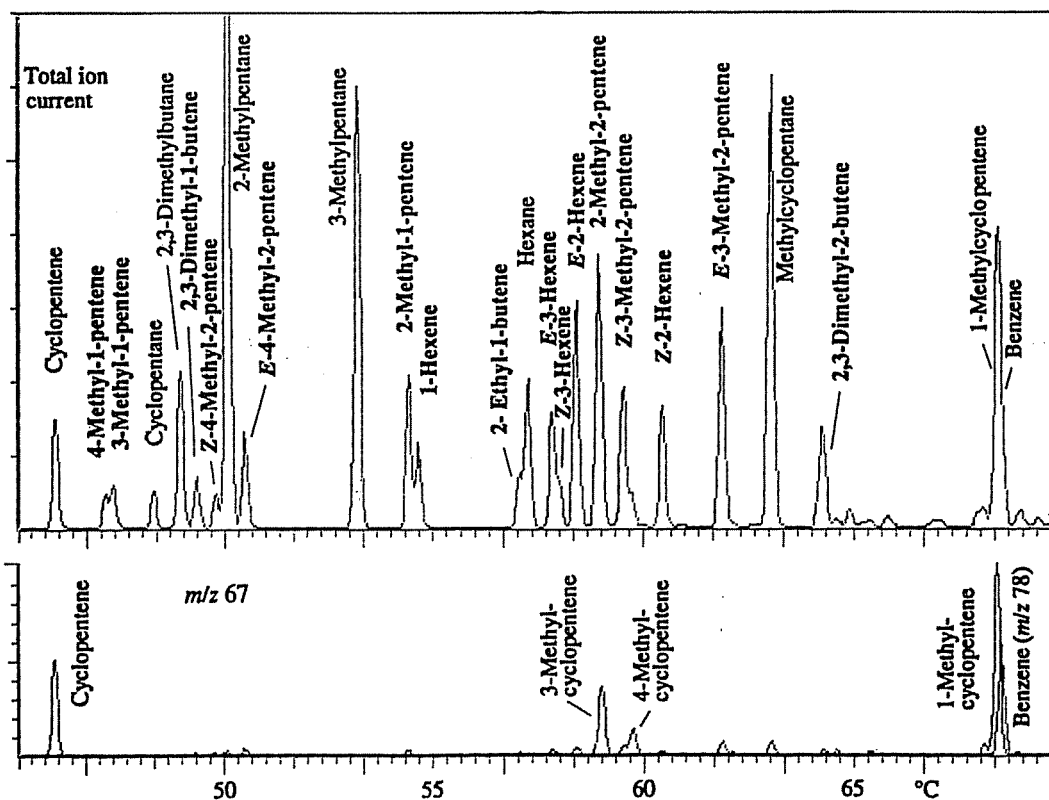


Figure 1

Separations (methylsilicone column) and hydrocarbon identities in the hexene range of the FCC naphtha; total ion chromatogram with 16 acyclic hexenes; single-ion chromatograms marking the incompletely resolved methylcyclopentenes (*m/z* 67, M-15) and benzene (*m/z* 78, M).