Gas chromatographic–mass spectrometric characterization of all acyclic C_5–C_7 alkenes from fluid catalytic cracked gasoline using polydimethylsiloxane and squalane stationary phases

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Abstract

Published retention indices of acyclic alkenes C_5–C_7 on squalane and polydimethylsiloxane as stationary phases were investigated, and reliable retention indices of alkenes from various sources were converted to separation systems used in a laboratory. Retention indices measured on available authentic commercial alkenes and on alkenic fraction of gasoline, published retention indices as well as means of GC–MS were used for verification of calculated retention indices. Retention of some gas chromatographic unseparated isomer pairs was obtained by mass spectrometric deconvolution using a specific single-ion monitoring. On the basis of these retention data, C_5–C_7 alkenes were identified and analyzed in the gasoline from fluid catalytic cracking. In the gasoline all 59 acyclic C_5–C_7 isomeric alkenes were determined at significantly different concentration levels. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Alkenes are important products of many crucial reactions and processes, respectively, such as catalytic and thermal cracking, pyrolysis, disproportionation, oligomerization, dehydrogenation, isomerization, etc. In the environment, alkenes represent contaminants mainly as anthropogenic emissions of volatile alkenes, which are unburnt fuel components [1]. Photooxidants are formed during atmospheric alkene reactions, and reaction rate differences play a role even between individual isomers. For example, the relative rates for reaction of individual acyclic hexenes with ozone in the air are in a range of 1:100 and the reaction rate increases sharply with the number of alkyl groups adjacent to the double bond [2]. For this reason, the petroleum industry is required to produce a gasoline with reduced harmful automobile exhaust emissions (alkene and aromatic compounds), and effective analytical methods are needed to ensure that these restrictions are met. These studies demand not only usual group determination but also component analysis of alkenes.

Most gas chromatographic measurements of alkene retention were accomplished using squalane as the stationary phase. Gas chromatographic (GC)

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retention behaviour of individual acyclic alkenes was studied up to C_{20}, however, that above C_8 was focused on straight-chain alkenes. Larger files of retention data of acyclic alkenes up to C_8 were published on squalane as the stationary phase by Tourres [3], Schomburg [4], Loewenguth and Tourres [5], Hively and Hinton [6], Soják and Bučinská [7] and Schurig [8]. Under conditions of highly-precise measurements, Rijks and Cramers [9] reported retention indices of 55 C_5–C_7 alkenes on squalane as the stationary phase. Retention indices of all 59 acyclic C_5–C_7 alkenes (six pentenes, 17 hexenes and 36 heptenes) on squalane and Ucon LB-550-X as stationary phases were published by Matukuma [10], however, retention indices for certain alkenes on squalane are significantly distinct from those published later by other authors. Recently we published gas chromatography–mass spectrometry (GC–MS) characterization of all acyclic 59 C_5–C_7 alkenes from fluid catalytic cracked (FCC) gasoline using squalane stationary phase [11]. The triple of isomeric hexenes and six pairs of heptenes were not separated in the squalane capillary column used.

Retention indices of acyclic C_5–C_7 alkenes on other stationary phases were not published as completely as on the squalane phase. Because of higher temperature stability of polydimethylsiloxane (PDMS) stationary phases, later they replaced squalane in GC hydrocarbon analyses. Published works were focused on obtaining alkene retention indices and establishing the library of retention data as well as on alkene analyses in gasoline. The larger bodies of retention indices of acyclic alkenes on PDMS phases are reported in Refs. [12–16]. Boneva and Dimov [12] measured Kováts retention indices on OV-101 dimethylsilicone for three pentenes, 12 hexenes and 23 heptenes, Laub and Purnell [14] published retention indices on OV-101 poly(dimethylsiloxane) for five pentenes, 11 hexenes and 21 heptenes, White et al. [15] measured linear temperature programmed retention indices on cross-linked 100% PDMS (Petrocol® DH) for six pentenes, 16 hexenes and 13 heptenes and retention indices for another 11 heptenes were calculated from data of Ref. [14], and Ramnäs et al. [16] published linear temperature programmed relative retentions on DB-1 methylsilicone for six pentenes, 17 hexenes and for

29 heptenes. Retention data for 3-ethyl-1-pentene on PDMS have not been published yet.

Because of the complex nature of gasoline, complete GC separation of all components is not possible. Buchanan [17] stated that the peak resolution and identification of olefinic gasoline mixtures above C_6 becomes extremely difficult with use of conventional single-column capillary gas chromatography. By multidimensional gas chromatography he obtained class and carbon number hydrocarbon information from C_4 through C_{11}. Compositional analysis of hydrocarbon groups in gasoline-range materials by multidimensional SFC–GC was reported by Chen et al. [1]. Using GC separation of fraction saturates/alkenes on DB-1 capillary column (100 m×250 μm I.D., 0.5 μm film), they obtained 182 peaks 45 of which were not identified, and GC–MS was used to confirm and identify many of the peaks in the gasoline including 31 acyclic C_5–C_7 alkenes. On HP-Ultra 1 (methylsilicone) column 450 m×200 μm I.D., 0.33 μm film with 1.3 million effective plates, Berger [18] differentiated 970 compounds up to naphthalene in a gasoline including 19 acyclic C_5–C_7 alkenes, analysis times exceeded 650 min using a temperature program, however, the column is inadequate to resolve all components present. Ramnäs et al. [16] analysed 52 acyclic C_5–C_7 alkenes including all pentenes and hexenes, and 29 heptenes in an alkene-rich petrol fraction from the refinery fluid catalytic cracking by GC–MS on DB-1 and Al_2O_3/KCl stationary phases.

Generally, the problem of identification of individual acyclic C_5–C_7 alkenes, mainly heptenes, in FCC gasolines is related to their multicomponentity on one hand, and the lack of standard alkene reference materials, absence or relatively poor reproducibility of published retention indices of alkenes in relation to very close retention of some isomers, few published alkene retention indices on preferred silicone stationary phases, as well as to limitations of GC–MS hyphenated techniques at identification of isomers on the other hand. Also the calculation methods of alkene retention indices using quantum chemical, connectivity and topological parameters [19–21] for identification of isomeric alkenes in complex mixtures are not adequately precise.

This work investigated the reproducibility of retention indices of acyclic C_5–C_7 alkenes on

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squalane and polydimethylsiloxane as stationary phases, and reliable retention indices of alkenes from various published sources were converted to the separation systems available in our laboratory with focusing on GC characterization of all 36 acyclic heptenes. Available authentic commercial alkenes, C_5–C_7 alkenic fraction of gasoline, published retention indices of alkenes as well as means of GC–MS were used for verification of calculated retention indices. Obtained retention indices of all acyclic C_5–C_7 alkenes were converted from squalane to polydimethylsiloxane stationary phase. On the basis of these retention and mass spectrometric data, all C_5–C_7 alkenes were characterized in the gasoline from fluid catalytic cracking.

2. Experimental

The gasoline fraction from the FCC process (Slovnaft, Bratislava, Slovakia) with boiling point up to 100 °C was used as a model mixture. C_5–C_7 alkenes from this model mixture were prepared using displacement liquid chromatography by fluorescence indicator adsorption method (FIA) [22].

The obtained alkenic fraction was separated by GC in a laboratory-prepared glass capillary column 93 m×250 μm I.D. dynamically coated with squalane (E. Merck, Darmstadt, Germany) as a stationary phase. The efficiency of this column was 126 000 effective plates for *n*-heptane with retention factor $k'=1.7$ at 30 °C. Carrier gas helium with inlet pressure 245 kPa and linear velocity 22.6 cm s^{-1} was used.

The retention indices of alkenes on PDMS stationary phase were measured using a Petrocol DH column 150 m×250 μm I.D., 1.0 μm film (Supelco, Bellefonte, USA). The efficiency of this column was 373 000 effective plates for *n*-heptane with retention factor $k'=8.01$ at 30 °C. Carrier gas hydrogen with inlet pressure 245 kPa and linear velocity 25 cm s^{-1} was used. This column was also temperature programmed from 30 to 200 °C at a rate of 1 °C min^{-1} immediately upon injection for determination of linear temperature programmed retention indices of alkenes.

Different carrier gases for measurements of acyclic alkene retention on squalane and PDMS column were used. Nevertheless, the effect of carrier gas type (He vs. H_2) on retention of acyclic alkenes is practically negligible (less than 0.05 i.u.) [23].

The GC–MS measurements of retention indices were performed on gas chromatograph Trace GC 2000 Series Thermoquest CE Instruments with flame ionization detector and Voyager GC–MS Thermoquest Finnigan in SCAN-mode as well as in SIM-mode. Mass spectral data were obtained by cyclic scanning from 15 to 200 mass units with a cyclic time of 0.2 s. Transfer line temperature was 200 °C. Quadrupole conditions were: electron energy 70 eV, emission current 150 μA and ion source temperature 150 °C. Each GC peak was inspected for constancy of MS pattern in order to detect possible overlapping compounds and to measure their retention data. The GC–MS/SIM chromatograms were obtained for pentenes at m/z 70, for hexenes at m/z 84 and for heptenes at m/z 98 as well as for some specific ions of isomers.

Seventeen heptenes as standard materials (Table 1) from various commercial sources were used for gas chromatographic study of retention of acyclic heptenes. Kováts retention indices of C_5–C_7 alkenes were measured in a temperature range of 25–70 °C with average repeatability ±0.04 index unit (i.u.) for the squalane column and ±0.03 i.u. for the PDMS column. The linear temperature programmed retention indices of C_5–C_7 alkenes on PDMS column were measured with average repeatability ±0.04 i.u.

3. Results and discussion

3.1. Gas chromatography

3.1.1. Retention of alkenes on squalane column

Squalane was chosen as a stationary phase for GC measurements of FCC gasoline due to the availability of retention indices published for the largest number of alkenes up to C_7, as well as of highly-precise retention indices for a great number of alkenes included. However, published retention indices for some alkenes on squalane differ between various reference sources. To explain these differences the retention index values for the major number of alkenes published particularly by Rijks and Cramers [9], Matukuma [10], and Tourres [3]

Table 1

Measured Kováts retention indices and their temperature coefficients on squalane and PDMS, linear temperature programmed retention indices on PDMS and values of retention indices differences on PDMS and squalane of all C_5–C_7 acyclic alkenes

Peak no.	Alkene		I_{30}^{P}	dI^{P}/dT	I_{30}^{S}	dI^{S}/dT	I_{PT}^{P}	ΔI_{30}^{P-S}
1	3-Methyl-1-butene		457.1	0.02	450.1	0.03	451.1	7.0
2	1-Pentene		489.0	0.00	481.1	0.02	486.5	7.9
3	2-Methyl-l-butene		495.6	−0.02	488.2	0.01	494.4	7.4
4	*E*-2-Pentene		507.6	−0.05	500.7	−0.01	506.6	6.9
5	*Z*-2-Pentene		515.3	−0.02	504.6	0.01	514.0	10.7
6	3,3-Dimethyl-1-butene		513.9	0.04	505.3	0.07	513.1	8.6
7	2-Methyl-2-butene		520.2	−0.01	513.8	0.00	518.6	6.4
8	4-Methyl-1-pentene		556.2	0.02	548.1	0.05	554.6	8.1
9	3-Methyl-1-pentene		557.6	0.05	549.7	0.08	556.5	7.9
10	*Z*-4-Methyl-2-pentene		567.5	−0.01	555.5	0.02	565.9	12
11	2,3-Dimethyl-1-butene		566.1	0.03	557.6	0.04	564.9	8.5
12	*E*-4-Methyl-2-pentene		570.4	−0.03	561.9	−0.01	568.7	8.5
13	2-Methyl-1-pentene		588.0	0.00	579.4	0.02	587.4	8.6
14	1-Hexene		589.0	0.00	581.5	0.02	588.4	7.5
15	2-Ethyl-1-butene		599.0	−0.01	592.1	0.01	599.0	6.9
16	*E*-3-Hexene		603.2	−0.01	592.1	−0.02	603.2	11.1
17	*Z*-3-Hexene		602.2	−0.05	592.1	0.02	601.6	10.1
18	*E*-2-Hexene		604.9	−0.03	596.8	−0.01	604.6	8.1
19	2-Methyl-2-pentene		607.3	−0.03	597.7	−0.01	607.0	9.6
20	*Z*-3-Methyl-2-pentene		610.2	0.03	601.8	0.03	611.0	8.4
21	*Z*-2-Hexene		614.0	0.01	602.7	0.03	614.5	11.3
22	4,4-Dimethyl-1-pentene	SM	610.4	0.04	602.3	0.09	611.0	8.1
23	*E*-3-Methyl-2-pentene		620.2	0.00	612.2	0.01	620.8	8.0
24	*E*-4,4-Dimethyl-2-pentene		625.5	−0.03	614.8	−0.01	625.9	10.7
25	2,3-Dimethyl-2-butene		630.4	0.03	624.2	0.03	632.0	6.2
26	3,3-Dimethyl-1-pentene		630.1	0.10	623.7	0.12	632.8	6.4
27	2,3,3-Trimethyl-1-butene	SM	633.3	0.09	626.0	0.11	636.2	7.3
28	*Z*-4,4-Dimethyl-2-pentene		642.0	0.08	633.3	0.11	644.9	8.7
29	3,4-Dimethyl-1-pentene		641.3	0.09	634.6	0.11	644.4	6.7
30	2,4-Dimethyl-1-pentene		645.9	0.04	636.2	0.07	648.1	9.7
31	*Z*-2-Methyl-3-hexene		651.9	0.00	639.9	0.10	653.4	12.0
32	2,4-Dimethyl-2-pentene		654.9	−0.05	641.2	−0.03	655.5	13.7
33	3-Methyl-1-hexene		650.2	0.05	643.1	0.07	652.6	7.1
34	3-Ethyl-1-pentene	SM	653.4	0.10	644.7	0.10	656.4	8.7
35	*E*-2-Methyl-3-hexene	SM	660.5	−0.04	647.4	−0.02	661.1	13.1
36	2,3-Dimethyl-1-pentene		657.6	0.07	648.3	0.10	660.5	9.3
37	5-Methyl-1-hexene		656.4	0.01	649.0	0.04	658.2	7.4
38	*Z*-4-Methyl-2-hexene		665.8	0.01	653.6	0.06	667.6	12.2
39	*E*-4-Methyl-2-hexene		665.8	0.03	655.4	0.04	667.6	10.4
40	4-Methyl-1-hexene	SM	663.3	0.04	655.6	0.06	665.6	7.7
41	2-Ethyl-3-methyl-l-butene	SM	665.8	0.04	658.3	0.04	667.6	7.5
42	*E*-5-Methyl-2-hexene	SM	668.0	−0.01	659.0	0.02	669.3	9.0
43	*Z*-5-Methyl-2-hexene		679.0	0.03	668.3	0.06	681.0	10.7
44	*Z*-3,4-Dimethyl-2-pentene		678.9	0.03	669.4	0.04	680.8	9.5
45	2-Methyl-1-hexene		685.9	−0.01	677.4	0.02	686.8	8.5
46	*E*-3,4-Dimethyl-2-pentene		687.6	0.01	677.4	0.03	688.6	10.2
47	1-Heptene	SM	688.6	−0.01	681.1	0.03	689.3	7.5

Table 1. Continued

Peak no.	Alkene		I^{P}_{30}	dI^{P}/dT	I^{S}_{30}	dI^{S}/dT	I^{P}_{PT}	ΔI^{P-S}_{30}
48	2-Ethyl-1-pentene		689.3	0.00	681.1	0.03	690.2	8.2
49	Z-3-Methyl-3-hexene	SM	694.6	0.00	684.0	0.02	695.1	10.6
50	E-3-Heptene	SM	698.4	−0.04	687.4	−0.01	697.9	11.0
51	Z-3-Heptene	SM	701.1	0.00	689.6	0.03	701.6	11.5
52	2-Methyl-2-hexene	SM	702.4	−0.02	691.0	0.00	702.4	11.4
53	E-3-Methyl-3-hexene		703.4	−0.03	691.2	−0.01	703.2	12.2
54	Z-3-Methyl-2-hexene	SM	701.4	0.04	692.0	0.05	702.4	9.4
55	3-Ethyl-2-pentene	SM	706.2	0.01	696.3	0.03	707.6	9.9
56	E-2-Heptene	SM	705.1	−0.03	698.2	0.00	705.0	6.9
57	E-3-Methyl-2-hexene	SM	709.2	0.01	699.5	0.03	710.9	9.7
58	Z-2-Heptene	SM	712.8	−0.01	702.1	0.04	714.4	10.7
59	2,3-Dimethyl-2-pentene		712.8	0.04	702.1	0.04	715.5	10.7

P, polydimethylsiloxane; S, squalane; SM, standard material; dI^{S}/dT from Ref. [9] and missing data from our measurements.

were assessed. On the basis of linear regression for retention indices from Ref. [9] and that measured in a prepared column coated with squalane for available standards of 17 heptenes, a coincidence with average standard deviation of 0.10 i.u. was obtained. The result shows that the prepared separation system gives retention index values practically identical with those in Ref. [9]. Hence, the retention indices of alkenes on squalane published in Ref. [9] were chosen as reference values for this study.

For evaluation of published retention indices of all acyclic alkenes to C_7 on squalane as a stationary phase [10] these were correlated with published data [9]. Such correlation as a relationship of the retention index difference $\Delta I^{S_{MR}}_{40}$ (superscripts R and M refer to Rijks author of Ref. [9] and Matukuma author of Ref. [10], respectively) of C_5–C_7 alkenes on squalane from Refs. [10] and [9] vs. their retention indices on squalane $I^{S_R}_{40}$ at 40 °C from Ref. [9] is shown in Fig. 1. It is obvious that the retention indices of alkenes obtained in these separation systems show systematic differences. The ΔI values increase with increasing alkene retention for pentenes, decrease for hexenes, and increase for heptenes. This unexpected behaviour is probably related to non-exact determination of retention of comparative standards in the retention index system during the measurement of retention indices of C_5–C_7 alkenes in Ref. [10], because the retention indices of n-alkenes from Ref. [9] are close to those in Refs. [3–7] and also to our measurements on available

alkene standards. There are significant deviations of ΔI values at pentenes for 3-methyl-1-butene 23 i.u., and at hexenes for 4-methyl-1-pentene 10 i.u. Comparison of other literary data from Tourres [3] and Hively and Hinton [6] confirmed deviations of retention indices on squalane for these alkenes from Ref. [10]. For heptenes, a greater deviation from linear dispersion of measured dependence on Fig. 1 of 3 i.u. is obtained for Z-3-methyl-2-hexene, how-
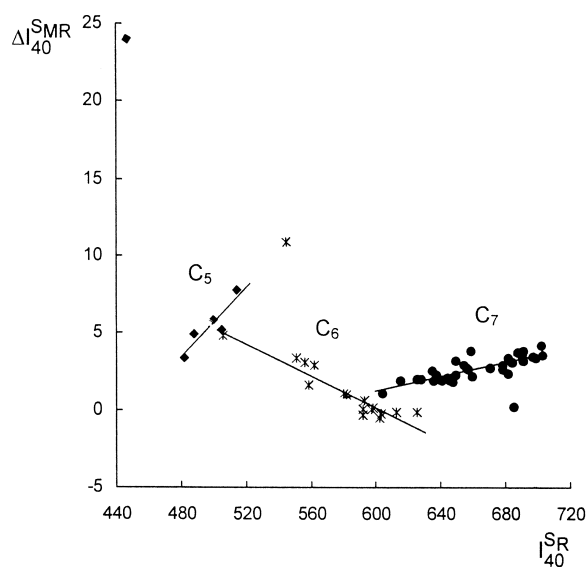

Fig. 1. The dependence of the retention index difference $\Delta I^{S_{MR}}_{40}$ of C_5–C_7 alkenes on squalane from Refs. [10] and [9] vs. their retention indices on squalane $I^{S_R}_{40}$ at 40 °C from Ref. [9].

ever the values of retention indices of this heptene are very similar not only in Refs. [8,9] but also in Refs. [5,6].

Correlation of congener retention with various types of compounds on two stationary phases found that isomers are placed on parallel linear regressions creating so-called isomer cluster phenomena [24]. The larger is the difference between stationary phase polarity, the more noticeable is the effect. Retention indices for 53 C_5–C_7 alkenes on squalane published by Rijks [9] and Matukuma [10] are correlated in Fig. 2. Erroneous retention data for three C_5–C_7 alkenes discussed above are not included. The iso-

mer cluster phenomena is not apparent on the graph because of the similarity of both stationary phases. All clusters of isomers approach each other and overlap as a single line with the standard deviation of 1.68 i.u. Fig. 2 illustrates also similar correlations of retention indices on squalane for isomeric pentenes, hexenes and heptenes. Calculated standard deviations for these relationships are: 0.77 for pentenes, 0.57 for hexenes, and 0.42 for heptenes. The values demonstrate that this correlation concept is more precise for isomeric alkenes than correlation including congeners of alkenes. Therefore, the corresponding linear regression equation for isomeric
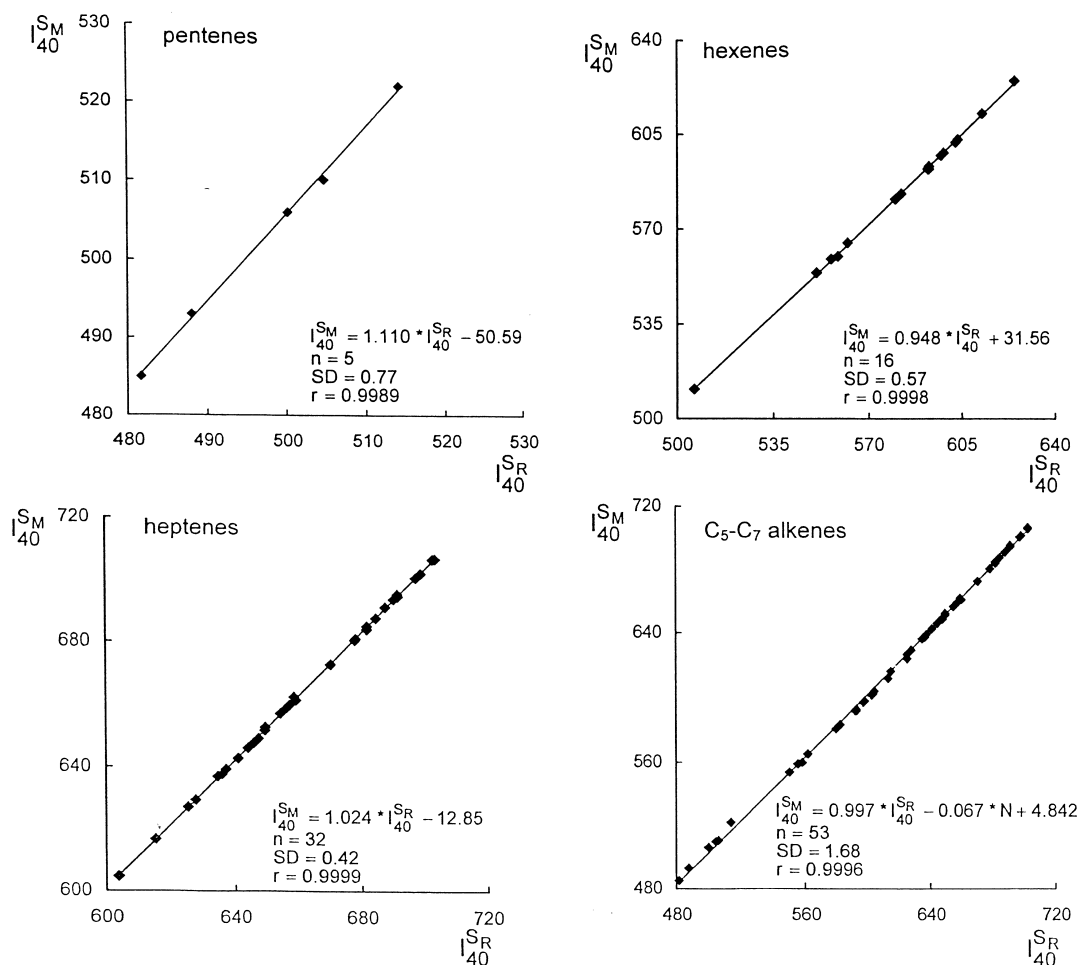

Fig. 2. Correlations of the retention indices of C_5–C_7 alkenes on squalane at 40 °C from Refs. [10] vs. [9]. N, number of alkene carbon atoms.

heptenes was employed for retention index calcula-
tions of four heptenes, Z-2-methyl-3-hexene, Z-5-
methyl-2-hexene, E-3-methyl-2-hexene and Z-2-hep-
tene, which were missing in the retention index data
in Ref. [9].

These calculated retention indices were compared
with published data from other references for Z-2-
heptene [7] and E-3-methyl-2-hexene [6] with good
agreement. Later, E-3-methyl-2-hexene was obtained
as a standard material and the measured retention
index was close to the calculated retention index for
the gasoline sample. Accurate retention indices of
the remaining two heptenes, Z-2-methyl-3-hexene
and Z-5-methyl-2-hexene, were obtained using GC–
MS/SIM system on the basis of retention index
measurement of these heptenes from the sample of

FCC gasoline, which contained all possible heptene
isomers. The differences of measured and published
[10] retention indices for these heptenes are 2.9 and
3.1 i.u. in agreement with the dependence on Fig. 1.

GC–MS/SIM chromatograms for separation of
pentenes at m/z 70, hexenes at m/z 84 and heptenes
at m/z 98 from the gasoline sample on the squalane
column at a temperature of 30 °C are given in Figs. 3
and 4. It is apparent that an abundant molecular ion
permits specific single-ion monitoring of the acyclic
pentenes, hexenes and heptenes in the gasoline
fraction. A single overlapping congener pair from
C_5–C_7 alkenes, specifically Z-2-pentene (*5*) and 3,3-
dimethyl-1-butene (*6*), was found only. Separation
of all six pentenes was obtained. For 16 possible
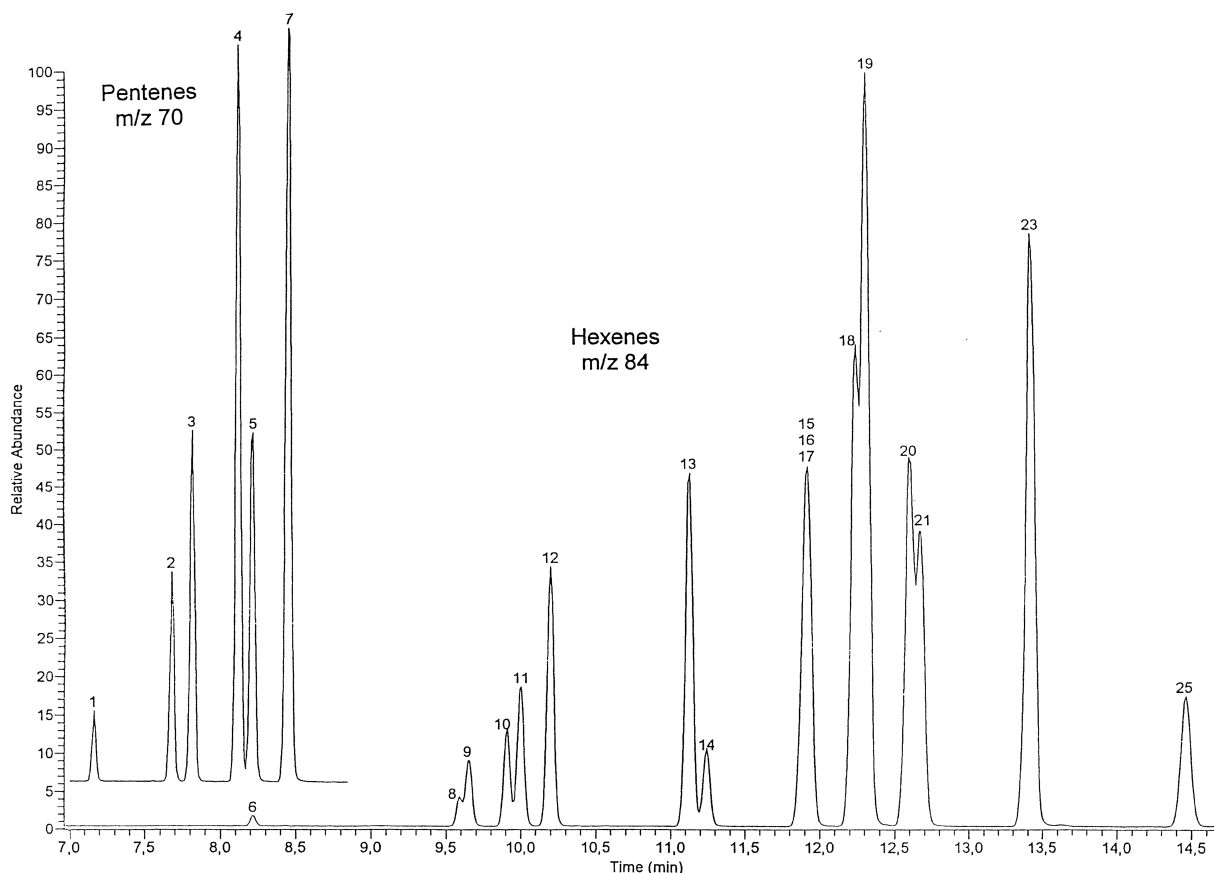hexenes only the triple, 2-ethyl-1-butene (*15*), E-3-

Fig. 3. GC–MS/SIM chromatograms of separation of acyclic pentenes and hexenes from the FCC gasoline on squalane column at 30 °C.
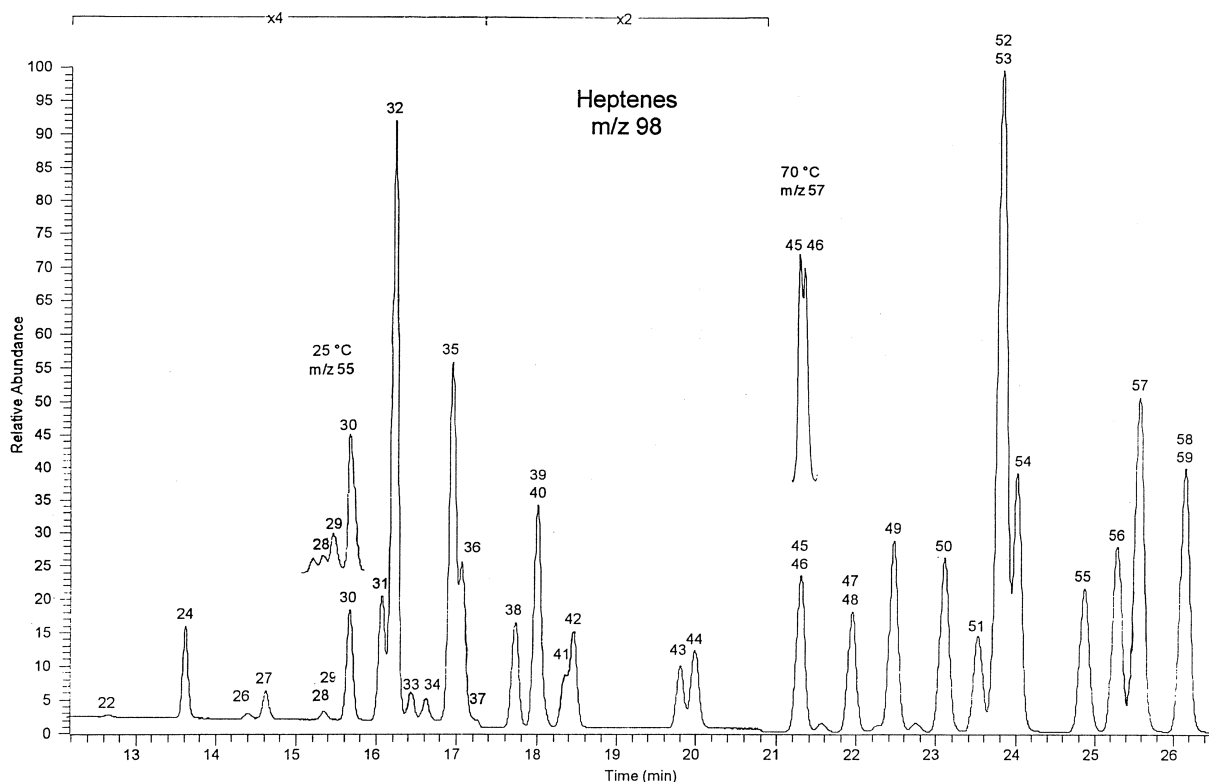Peak identification as in Table 1.

Fig. 4. GC–MS/SIM chromatogram of separation of acyclic heptenes from the FCC gasoline on squalane column at 30 °C. Peak identification as in Table 1.

hexene (*16*) and *Z*-3-hexene (*17*), is not separated; their partial resolution can be obtained by separation at 20 and 70 °C, respectively [9]. Mass spectrometric deconvolution of 2-ethyl-1-butene (*15*) from the pair *E*-3-hexene (*16*), *Z*-3-hexene (*17*) by measurement at m/z 56 and column temperature 25 °C was obtained (Fig. 5a). In case of separation of 36 possible heptene isomers, six pairs are not separated in the squalane capillary column at 30 °C: 2,3-dimethyl-1-pentene (*36*) and 5-methyl-1-hexene (*37*), 4-methyl-1-hexene (*40*) and *E*-4-methyl-2-hexene (*39*), *E*-3,4-dimethyl-2-pentene (*46*) and 2-methyl-1-hexene (*45*), 1-heptene (*47*) and 2-ethyl-1-pentene (*48*), 2-methyl-2-hexene (*52*) and *E*-3-methyl-3-hexene (*53*), 2,3-dimethyl-2-pentene (*59*) and *Z*-2-heptene (*58*). Heptenes not separated by gas chromatography were mass spectrometrically inspected using the specific single-ion monitoring on the basis of mass spectrometric data of the library of the GC–MS system used and Ref. [26]. The presence of 3,4-

dimethyl-1-pentene (*29*) and 5-methyl-1-hexene (*37*) in gasoline is not apparent in Fig. 4 because of their low abundance at m/z 98. A change of m/z at squalane column temperature 30 °C to m/z 55 and m/z 57 resulted in deconvolution of 3,4-dimethyl-1-pentene (*29*) and 5-methyl-1-hexene (*37*), respectively, thus their presence in the gasoline sample was ascertained (Fig. 5b and c). Similarly, deconvolution of the pairs *E*-4-methyl-2-hexene (*39*), 4-methyl-1-hexene (*40*) at 30 °C and 2-methyl-2-hexene (*52*), *E*-3-methyl-3-hexene (*53*) at 26 °C was obtained at m/z 57, and at m/z 55, respectively (Fig. 5d and e). Deconvolution of the pair *Z*-2-heptene (*58*), 2,3-dimethyl-2-pentene (*59*) was obtained by measurement at column temperature 70 °C and m/z 56 and 83 (Fig. 5f). Thus, 1-heptene (*47*), 2-ethyl-1-pentene (*48*) is the only unresolved pair of heptenes on the squalane column because of equal retention in the measured temperature range [9], and also the means of single-ion monitoring are not useful. Retention
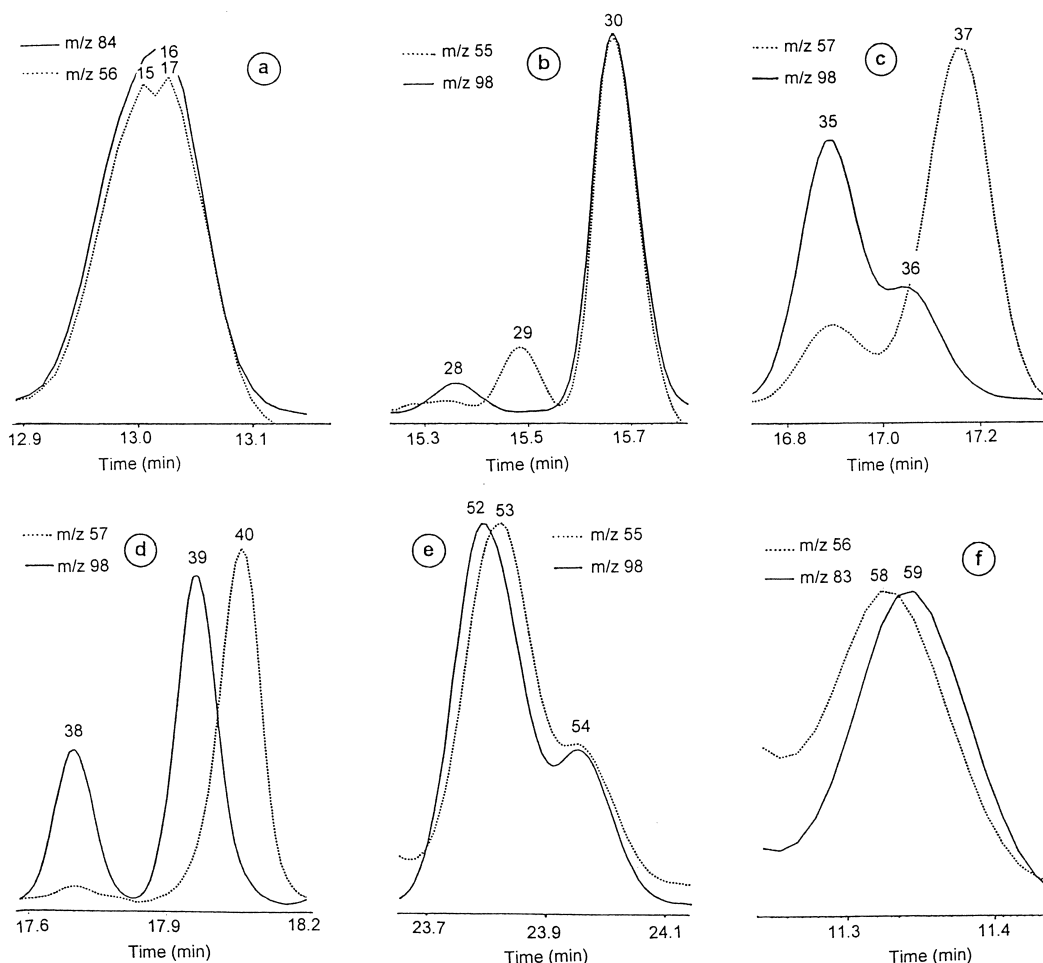
Fig. 5. Mass spectrometric deconvolution of gas chromatographic unseparated hexene and heptene isomers on squalane column at (a) 25 °C, (b, c, d) 30 °C, (e) 26 °C, (f) 70 °C using a specific single-ion monitoring. Peak identification as in Table 1.

times of deconvoluted alkenes obtained by mass spectrometric deconvolution of chromatographic un-separated heptenes were used for calculation of their retention indices.

The measured Kováts retention indices of acyclic C_5–C_7 alkenes on squalane column at 30 °C and their temperature coefficients are given in Table 1.

3.1.2. Retention of alkenes on PDMS column

Similar procedures as for squalane column were used for obtaining alkene retention characteristics on PDMS column. However, the number of published Kováts retention indices of alkenes on PDMS phase was lower and also linear programmed retention

indices of alkenes were published, which are less reproducible than isothermic retention indices. More-over, comparison of measured retention indices on authentic commercial alkenes with several published data [12,14–16] for PDMS phases showed signifi-cant differences. On the other hand, the obtained retention indices of all C_5–C_7 alkenes and quantita-tively characterized model mixture of studied alkenes from FCC gasoline and measured mass spectra on squalane column facilitated the alkene characteriza-tion on PDMS column.

The obtained GC–MS/SIM chromatograms of separation of pentenes at m/z 70, hexenes at m/z 84 and heptenes at m/z 98 on PDMS stationary phase

are given in Figs. 6 and 7. Similarly to squalane column separation the same overlapping C_5–C_7 alkene congener pair particularly Z-2-pentene (*5*) and 3,3-dimethyl-1-butene (*6*) was found.

Comparison with separation of alkenes on squalane column (Figs. 3 and 4) suggests that separation on the PDMS column is better. This is not only due to the higher efficiency of the PDMS column. Table 2 gives selectivity factors as relative retention of the last and first eluted isomers for pentenes, hexenes and heptenes on squalane and PDMS stationary phases at 30, 40 and 60 °C. It is clear that isomeric selectivity as the range of alkene isomers' retention is greater for a squalane phase. Better separation of alkene isomers on the PDMS column also results from different activity coefficients of alkene isomers on the stationary phases used, hence, more uniform distribution of alkene isomers' retention on the PDMS column. It leads to a

different retention order of many heptene isomers on both columns at equal column temperature.

On the PDMS column the separation of all isomeric pentenes and hexenes was obtained at 30 °C. In case of separation of heptenes at 30 °C, at m/z 98 triplet Z-4-methyl-2-hexene (*38*), E-4-methyl-2-hexene (*39*), 2-ethyl-3-methyl-1-butene (*41*), and the pairs Z-5-methyl-2-hexene (*43*), Z-3,4-dimethyl-2-pentene (*44*), and Z-3-heptene (*51*), Z-3-methyl-2-hexene (*54*), and Z-2-heptene (*58*), 2,3-dimethyl-2-pentene (*59*) are chromatographically unseparated. The presence of 3,4-dimethyl-1-pentene (*29*) was confirmed by measurement at m/z 55 (Fig. 8a). The mass spectrometric deconvolution of the pair Z-5-methyl-2-hexene (*43*), Z-3,4-dimethyl-2-pentene (*44*) was realized by measurement at m/z 55 and 83. Fig. 8b shows that the index difference of these heptenes is 0.09 i.u. In this case, the GC system used resolves two isomers with $\delta I \gtrsim 1$ i.u. and
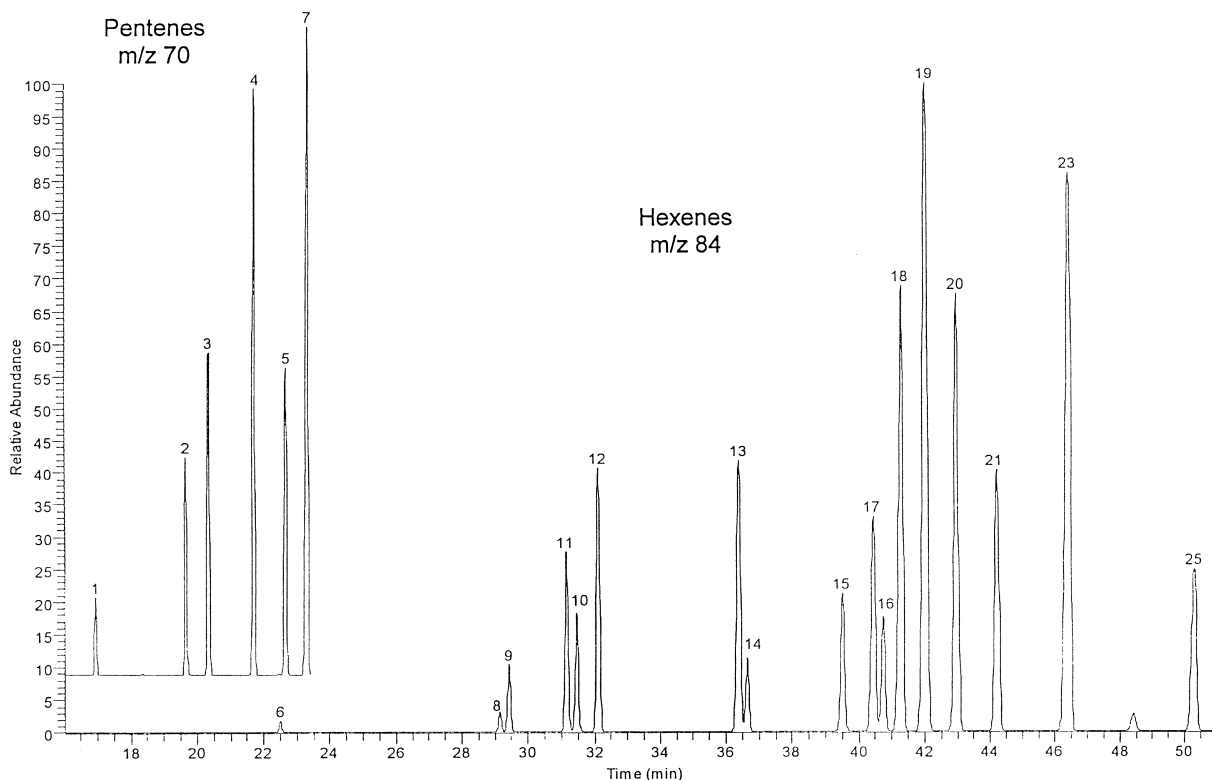

Fig. 6. GC–MS/SIM chromatograms of separation of acyclic pentenes and hexenes from the FCC gasoline on the PDMS column at 30 °C. Peak identification as in Table 1.
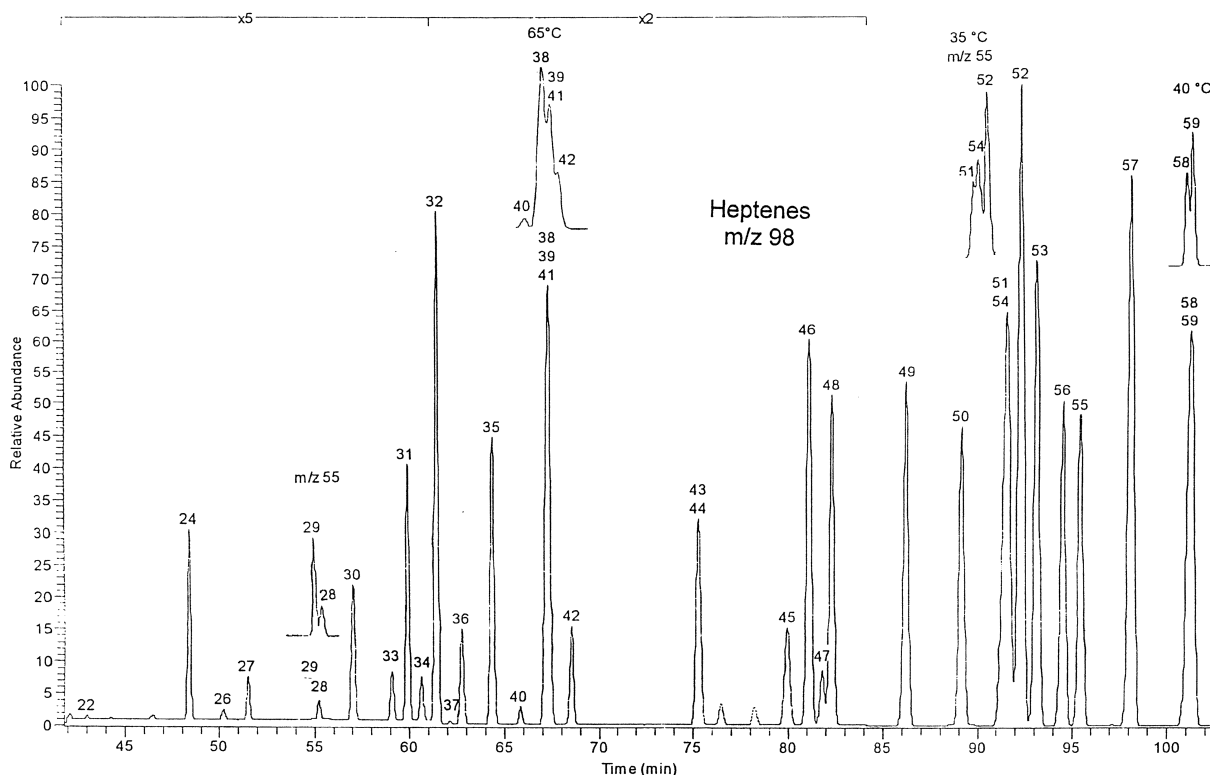
Fig. 7. GC–MS/SIM chromatogram of separation of acyclic heptenes from the FCC gasoline on PDMS column at 30 °C. Peak identification as in Table 1.

GC–MS/SIM system with $\delta I \gtrsim 0.1$ i.u. With a temperature change to 40 °C, and 60 °C, the gas chromatographic separation of pair Z-2-heptene (*58*), 2,3-dimethyl-2-pentene (*59*), and separation of Z-4-methyl-2-hexene (*38*) from the pair E-4-methyl-2-hexene (*39*), 2-ethyl-3-methyl-1-butene (*41*) was obtained, respectively. Separation of the pair Z-3-heptene (*51*), Z-3-methyl-2-hexene (*54*) was ob-

Table 2
Selectivity factors as relative retention of the last and first eluted isomers for pentenes, hexenes and heptenes on PDMS and squalane at 30, 40 and 60 °C

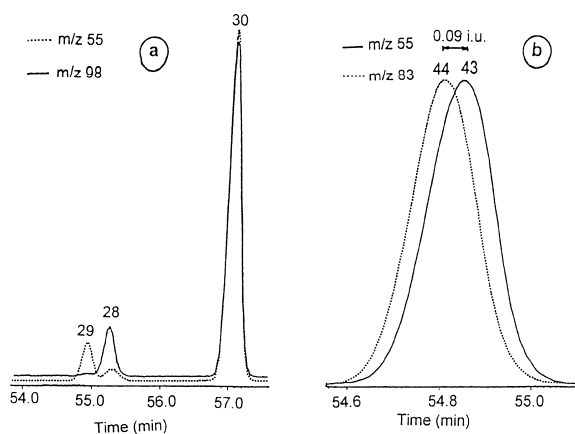|	PDMS			Squalane		
	30 °C	40 °C	60 °C	30 °C	40 °C	60 °C
C5	1.92	1.85	1.73	2.12	2.04	1.89
C6	3.23	3.02	2.68	3.82	3.56	3.11
C7	2.76	2.61	2.45	3.04	2.84	2.58

Fig. 8. Mass spectrometric deconvolution of gas chromatographic unseparated heptene isomers on a PDMS column at (a) 30 °C, (b) 40 °C using a specific single-ion monitoring. Peak identification as in Table 1.

tained by measurement at 35 °C at m/z 55. Thus, only the pair *E*-4-methyl-2-hexene (*39*), 2-ethyl-3-methyl-1-butene (*41*) is not resolved on the PDMS column employed. However, the analytical information on all C_5–C_7 acyclic alkenes was obtained through the combination of chromatographic data from both columns used.

The transfer of retention indices of alkenes measured on squalane to PDMS was described on the basis of linear regression equation [12,25]. Correlations of the measured retention indices of all C_5–C_7 acyclic alkenes on PDMS vs. squalane stationary phases are shown in Fig. 9. The corresponding linear

regression equations are characterized by the average standard deviation of 1.7 i.u. Measured retention indices of alkenes on PDMS at 30 °C are by 6.2 to 13.7 i.u. greater than those on squalane (Table 1). It means that the retention indices of acyclic C_5–C_7 alkenes are significantly different on PDMS and squalane stationary phases, therefore, conversion of the retention indices of alkenes from squalane to PDMS stationary phase through linear regression equation is inappropriate for identification of the complex mixture of alkene isomers. The obtained relative great retention differences of isomers on squalane and PDMS correspond with different re-
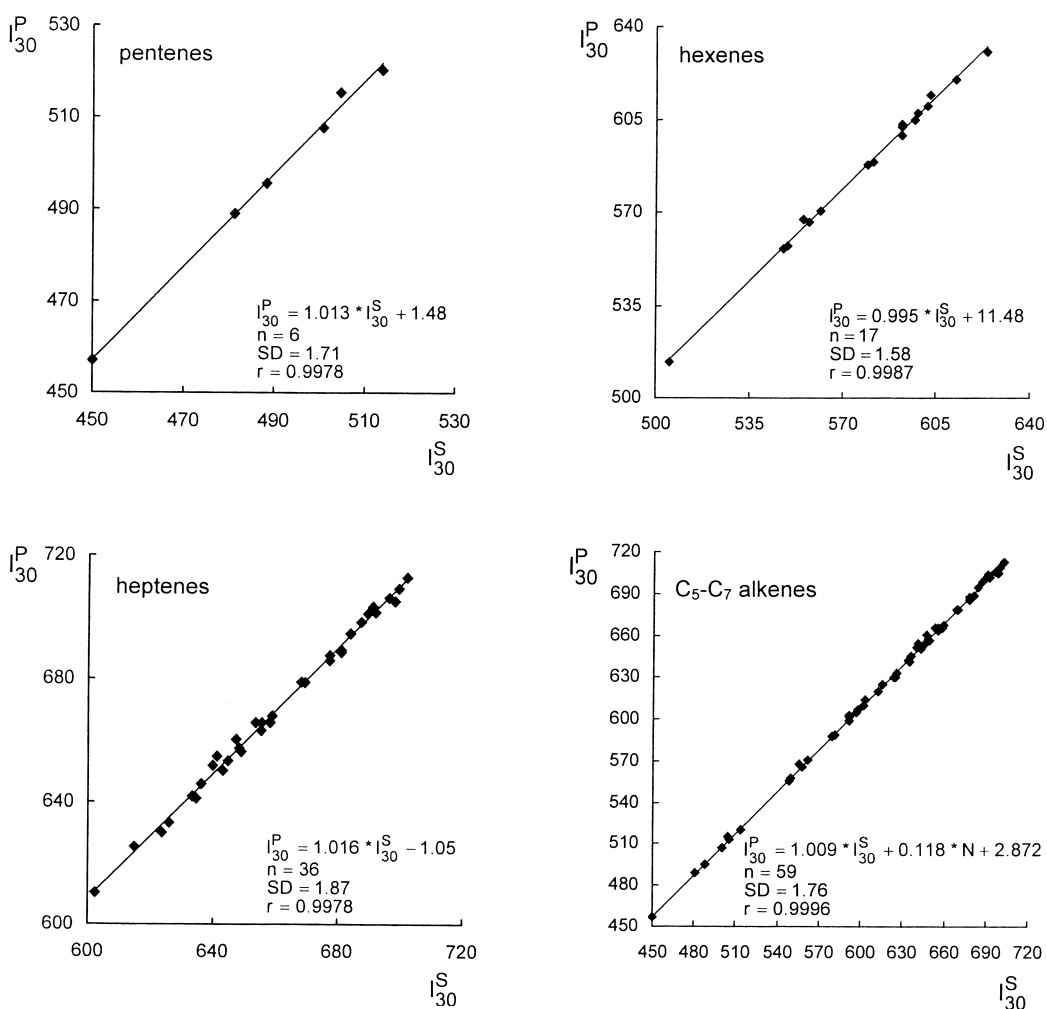

Fig. 9. Correlations of the measured retention indices of all C_5–C_7 alkenes on PDMS vs. squalane stationary phases at 30 °C. *N*, number of alkene carbon atoms.

tention order of a relatively great number of heptene isomers on both stationary phases studied. The dependence of ΔI values on the molecular structure of acyclic alkenes is rather complex. For example, the acyclic C_5–C_7 alkenes exist in 14 Z-/E-isomeric pairs. In eight such isomeric pairs the Z-isomers exhibit higher ΔI values, while in the remaining six pairs the E-isomers were observed at the higher ΔI values. Most different ΔI values were found between congeners 2,3-dimethyl-2-butene (6.3 i.u.) and 2,4-dimethyl-2-pentene (13.7 i.u.), and between Z-/E-isomers for Z-2-pentene (10.8 i.u.) and E-2-pentene (6.9 i.u.). The knowledge of ΔI values is useful for identification of isomeric acyclic octenes on the PDMS stationary phase.

Measured Kováts retention indices and their temperature coefficients and linear temperature programmed retention indices of all C_5–C_7 alkenes on PDMS column as well as values of retention indices differences on PDMS and squalane ΔI^{P-S} are given in Table 1. Comparison of measured and published [11,13] retention indices' differences shows greater deviations (>2 i.u.) for Z-4-methyl-2-hexene (6.5 i.u.), Z-3-heptene (5.6 i.u.), E-3-heptene (4.1 i.u.), 2-methyl-2-hexene (3.5 i.u.), Z-3,4-dimethyl-2-pentene (3.0 i.u.), 2,3-dimethyl-2-pentene (2.8 i.u.) and for E-2-heptene (−4.1 i.u.). These differences can be explained by the fact that published retention indices [12] were not measured on authentic commercial alkenes. Measured linear temperature programmed retention indices are in agreement on 1 i.u. with Ref. [16] except for 2-ethyl-3-methyl-1-butene (16 i.u.), E-3-methyl-3-hexene (8 i.u.) and for Z-2-methyl-3-hexene (−14 i.u.). In comparison with linear temperature programmed retention indices in Ref. [15] the differences range approximately from zero for isomers eluting near to retention of n-alkane to 9 i.u. for isomers eluted in the middle between neighbouring alkanes except for E-3-methyl-3-hexene, which deviates from this dependence by about 10 i.u.

3.2. Mass spectrometry

The possibilities of GC–MS for structural identification of acyclic C_5–C_7 alkenes from FCC gasoline including 29 heptenes were briefly discussed in Ref. [16]. Specific fragmentation of some C_5–C_7 alkenes was described, however, the mass spectra of several

isomers were found to be very similar. Eight peak index mass spectra of 28 isomers of heptene were published in Ref. [26], and the library of the GC–MS system used contains the mass spectra for 35 acyclic heptenes. From the published mass spectral data, only the spectrum of 2-ethyl-1-pentene was unknown. Nevertheless, 2-ethyl-1-pentene is present in the model sample of FCC gasoline, and on the PDMS column it is separated from other heptenes.

Our mass spectrometric study was focused on confirmation of gas chromatographic identification of acyclic heptenes. Under electron impact (EI, 70 eV) working conditions in the positive-ion mode, the mass spectra of all gas chromatographic peaks on PDMS and squalane columns were recorded. The mass spectra of heptenes were compared with reference spectra and interpreted with respect to mass spectrometric fragmentation. The five most intense peaks detectable in the range of m/z 40 to 98 considered to be of specific value for structural assignment by their m/z values are reported in Table 3.

The molecular ions M^+ (m/z 98) were observed for all isomeric heptenes in the wide range of relative abundances (RA) from 1% for 5-methyl-1-hexene up to 61% for E-3-heptene. It was found that both monosubstituted alkyl hexenes-1 and disubstituted alkyl pentenes-1 have weak RA% of M^+. The reason is that such isomers can produce stable fragments and/or alkyl radicals from allylic cleavage of molecular ions. On the contrary, both straight-chain Z-/E-heptene isomers and isomers with a double bond in the position 2- and 3- have rather stronger RA% of M^+. In this case, the fragments and alkyl radicals formed by allylic cleavage might be relatively unstable.

McLafferty rearrangement was often observed for several heptenes followed by a hydrogen shift with the loss of an alkene moiety and resulting in specific even mass ions at m/z 70, 56 and 42.

The fragments at m/z 83, 69, and 55 were observed as a base peak. The fragment at m/z 83 is formed by the loss of methyl radical $CH_3^{\cdot}$ from molecular ion mostly in isomers possessing tert-butyl or isopropyl branching at the double-bonded carbon atom. The fragment m/z 69 is formed by loss of ethyl radical $C_2H_4^{\cdot}$ from molecular ion in isomers having ethyl and/or propyl branch at the double-

Table 3
Mass spectral data of all acyclic heptenes

Peak no.	Alkene	M^+ RA (%)	Specific MS ions m/z				
50	*E*-3-Heptene	61	41 (100)	56 (98)	69 (90)	55 (76)	98 (61)
51	*Z*-3-Heptene	40	41 (100)	56 (80)	69 (68)	55 (62)	98 (40)
54	*Z*-3-Methyl-2-hexene	37	41 (100)	69 (98)	55 (58)	98 (37)	56 (23)
56	*E*-2-Heptene	59	55 (100)	56 (99)	41 (65)	69 (63)	98 (59)
33	3-Methyl-1-hexene	8	55 (100)	69 (97)	41 (73)	56 (71)	70 (53)
28	*Z*-4,4-Dimethyl-2-pentene	34	55 (100)	83 (94)	41 (36)	98 (34)	43 (18)
46	*E*-3,4-Dimethyl-2-pentene	45	55 (100)	83 (93)	98 (45)	41 (25)	69 (10)
59	2,3-Dimethyl-2-pentene	59	55 (100)	83 (80)	98 (59)	41 (33)	69 (20)
44	*Z*-3,4-Dimethyl-2-pentene	46	55 (100)	83 (77)	98 (46)	56 (37)	41 (33)
45	2-Methyl-1-hexene	5	56 (100)	41 (39)	70 (22)	55 (20)	69 (13)
30	2,4-Dimethyl-1-pentene	7	56 (100)	43 (36)	41 (33)	55 (26)	70 (19)
37	5-Methyl-1-hexene	1	56 (100)	55 (52)	41 (49)	57 (37)	70 (22)
58	*Z*-2-Heptene	54	56 (100)	55 (89)	41 (77)	69 (65)	98 (54)
47	1-Heptene	12	56 (100)	55 (69)	41 (60)	70 (44)	42 (36)
43	*Z*-5-Methyl-2-hexene	13	56 (100)	55 (67)	43 (58)	41 (44)	70 (30)
42	*E*-5-Methyl-2-hexene	14	56 (100)	55 (77)	43 (50)	41 (36)	70 (27)
29	3,4-Dimethyl-1-pentene	2	56 (100)	55 (85)	70 (73)	41 (57)	43 (56)
40	4-Methyl-1-hexene	6	56 (100)	57 (99)	41 (67)	55 (25)	70 (18)
22	4,4-Dimethyl-1-pentene	3	57 (100)	41 (60)	55 (51)	83 (23)	70 (5)
34	3-Ethyl-1-pentene	23	69 (100)	41 (87)	55 (36)	70 (28)	56 (22)
26	3,3-Dimethyl-1-pentene	5	69 (100)	41 (60)	55 (40)	70 (17)	83 (17)
36	2,3-Dimethyl-1-pentene	14	69 (100)	41 (76)	55 (50)	70 (37)	83 (25)
39	*E*-4-Methyl-2-hexene	27	69 (100)	41 (61)	55 (47)	98 (27)	56 (18)
38	*Z*-4-Methyl-2-hexene	18	69 (100)	41 (54)	55 (34)	98 (18)	70 (13)
52	2-Methyl-2-hexene	40	69 (100)	41 (43)	98 (40)	55 (23)	56 (20)
57	*E*-3-Methyl-2-hexene	50	69 (100)	41 (68)	98 (50)	55 (43)	70 (26)
31	*Z*-2-Methyl-3-hexene	34	69 (100)	55 (78)	41 (64)	56 (48)	98 (34)
35	*E*-2-Methyl-3-hexene	35	69 (100)	55 (79)	41 (52)	56 (42)	98 (35)
41	2-Ethyl-3-methyl-1-butene	38	69 (100)	55 (82)	41 (54)	83 (40)	98 (38)
49	*Z*-3-Methyl-3-hexene	42	69 (100)	55 (62)	41 (47)	98 (42)	56 (15)
55	3-Ethyl-2-pentene	60	69 (100)	55 (83)	98 (60)	41 (48)	56 (23)
53	*E*-3-Methyl-3-hexene	41	69 (100)	55 (56)	98 (41)	41 (36)	83 (13)
48	2-Ethyl-1-pentene	43	70 (100)	55 (96)	41 (71)	69 (64)	98 (43)
24	*E*-4,4-Dimethyl-2-pentene	39	83 (100)	55 (74)	41 (42)	98 (39)	56 (12)
27	2,3,3-Trimethyl-1-butene	26	83 (100)	55 (82)	41 (37)	98 (26)	56 (12)
32	2,4-Dimethyl-2-pentene	40	83 (100)	55 (88)	98 (40)	41 (25)	43 (11)

bonded carbon atom. In addition m/z 69 fragments are formed by allylic cleavage of molecular ion with the loss of ethyl radical. The m/z 55 fragments are produced by allylic cleavage of molecular ion with the loss of *n*-propyl radical $C_3H_7^{.}$. The loss of $C_3H_7^{.}$ radical in most heptenes appeared to be the result of the consecutive loss of $CH_3^{.}$ and $C_2H_4^{.}$ radicals rather than a one-step loss of $C_3H_7^{.}$ radical.

Unlike the results in Ref. [16] the GC–MS/SIM chromatograms of heptenes in Figs. 4, 5, 7 and 8 confirm the presence of seven heptenes (no. 22, 24, 26, 27, 28, 29 and 34) in small amounts, i.e.

trimethyl substituted butene, dimethyl substituted pentenes and 3-ethyl-1-pentene in the FCC gasoline.

4. Conclusion

The retention indices of acyclic C_5–C_7 alkenes on squalane and polydimethylsiloxane stationary phases that were unreliable or missing in the literature were measured and completed. Conversion of retention indices of alkenes from squalane to polydi-methylsiloxane stationary phase using a linear re-

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gression equation is not adequately precise for identification of isomeric alkenes. In most cases the use of GC–MS hyphenation for confirmation of isomeric alkene identification is possible only in combination with gas chromatographic retention data because the mass spectra of some isomers are very similar. On the other hand, the difference in abundance of some specific single-ions of isomers allows mass spectrometric deconvolution of alkene pairs that are not separated by gas chromatography. Primarily, the presence of all 59 acyclic C_5–C_7 alkenes in FCC gasoline was determined.

Acknowledgements

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