

STRUCTURE-PROPERTY ANALYSIS OF OCTANE NUMBERS FOR
HYDROCARBONS (ALKANES, CYCLOALKANES, ALKENES)

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(received. August 1991)

Abstract. Correlations between the chemical structure of hydrocarbons and their posted octane numbers ($PON = MON/2 + RON/2$) have been tested separately for 45 alkanes, 35 cycloalkanes and 75 alkenes. In the first group the statistical results are better ($r^2 = 0.92$) than in the second ($r^2 = 0.78$) and third groups ($r^2 = 0.80$) because of the variation range of PON values.

Introduction

It has long been known that the anti-knock properties of hydrocarbons depend on their chemical structure. Qualitatively, alkanes with higher branching degree have better anti-knock properties than the less branched ones; aromatic hydrocarbons have even better properties than branched alkanes in this respect. Alkenes and cycloalkanes also have better properties than alkanes with the same skeleton, and carbon count, respectively.

In the automotive industries using internal combustion engines with spark-plug initiation, there has been a continuous trend for increasing the compression ratio, leading in turn to higher requirements for anti-knock properties of gasoline.

The quantitative measurement of anti-knock properties of fuel is effected by comparison with standardized binary mixtures of n-heptane and isooctane or 2,4,4-trimethylpentane. The percent by volume of isooctane in the binary mixture is the "octane number"(ON); by definition, the octane numbers for n-heptane and isooctane are 0 and 100, respectively. For aviation fuels a third standard is used, namely isooctane plus 6 ml Et₄Pb/gallon with ON = 120.3.

A given gasoline is tested for incipient knocking sound of specific intensity at a certain compression ratio; then the percent of isooctane in a binary mixture of isooctane and n-heptane leading to knocking under the same conditions constitutes the octane rating of the given gasoline.

Since the beginning, two basic octane ratings have been in use for assessing the knocking characteristics of gasolines: the research octane number (RON) and the motor octane number (MON). Both can be measured experimentally in the same standardized

single-cylinder engine but under different operating conditions: at 600 rotations per minute (rpm) for RON, i.e. under low-severity engine operation, and at 900 rpm for MON, i.e. under severe conditions closer to those actually occurring on the road. The corresponding standardized tests are ASTM D-2699 and ASTM D-2700, respectively. In addition to these scales, a few other ones are employed: the posted octane number is the arithmetical average of the above two scales, $PON = (MON + RON)/2$; this scale is posted on gasoline pumps in service stations, and is also called anti-knock index; the road octane number is determined in specially equipped automobiles under actual road conditions; as expected, road octane numbers correlate much closer to MON than RON; blending octane numbers (again of MON or RON type) are used by refineries in order to arrive at calculable octane ratings by mixing (blending) known volumes of specific hydrocarbons, since the "actual" octane numbers enumerated above do not blend linearly; most companies have developed their own blending scales, therefore variations may be encountered according to the source. In the present paper we shall employ data provided in ref.¹ which differ slightly from those used in earlier work.

Octane numbers measured in the absence of tetraalkyllead additives are called clear octane numbers.

Generally, MON ratings are lower than RON ratings, and actual ones are lower than blending ones¹, as seen in Table 1.

The difference RON-MON is called octane sensitivity; for pure hydrocarbons, it is almost always a positive number ranging from 0 to 15; for gasolines a low octane sensitivity is desirable.

Table 1. Clear Octane numbers of pure hydrocarbons

	ACTUAL		BLENDING	
	RON	MON	RON	MON
<u>Alkanes C_nH_{2n+2}</u>				
n-C ₅	62	62	62	67
2-Me-C ₄	92	90	90	104
2,2-Me ₂ C ₃	85	80	100	90
n-C ₆	25	26	19	22
2,2-Me ₂ -C ₄	92	93	89	97
n-C ₇	0	0	0	0
2,2-Me ₂ -C ₅	93	96	89	93
2,2,3-Me ₃ -C ₄	>100	>100	113	113
2,2,4-Me ₃ -C ₅	100	100	100	100
2,2,3-Me ₃ -C ₅	100	100	105	112
<u>Alkenes C_nH_{2n}</u>				
1-en-C ₅	91	77	152	135
2-Me-2-en-C ₅	97	85	176	141
3-Me-2-en-C ₅	97	81	130	118
4-Me-2-en-C ₅	99	84	130	128
<u>Aromatics C_nH_{2n-6}</u>				
C ₆ H ₆	>100	>100	99	91
Me-C ₆ H ₅	>100	>100	124	112
1,2-Me ₂ -C ₆ H ₄	>100	>100	120	103
1,3-Me ₂ -C ₆ H ₄	>100	>100	145	124
1,4-Me ₂ -C ₆ H ₄	>100	>100	146	127
1,3,5-Me ₃ -C ₆ H ₃	>100	>100	171	137
Et-C ₆ H ₄	>100	98	124	107
Pr-C ₆ H ₄	>100	98	127	129
iPr-C ₆ H ₄	>100	99	132	124
<u>Cycloalkanes C_nH_{2n}</u>				
C ₅	101	85	141	141
Me-C ₅	91	80	107	99
C ₆	83	77	110	97
Me-C ₆	75	71	107	84
1,2-Me ₂ -C ₆	81	79	85	83
1,3-Me ₂ -C ₆	67	64	67	65
1,4-Me ₂ -C ₆	68	65	66	63

In order to increase the anti-knock resistance of the fuel, addition of small amounts of tetraethyllead (0.3 to 3 ml per gallon) was the method employed since 1922; however, the ecological and medical problems caused by lead in exhaust gases, as well as the fact that lead is poisoning not only living organisms but also the platinum catalysts used in catalytic converters for complete oxidation of the fuel to carbon dioxide, has led since 1975 to a development of alternative means for increasing anti-knock fuel resistance. Such methods are:

- reducing the amount of non-branched paraffins by selective extraction, or by crystallization on cooling;
- catalytic reforming which converts alkanes into aromatics;
- adding fuels with higher octane numbers such as isooctane (synthesized from isobutane and isobutene by alkylation), or oxygenated compounds such as ethanol, aromatics, methanol, or t-butyl methyl ether (MTBE).

The degree to which the octane rating of a gasoline increases on adding an octane boosting additive is called octane response and lead susceptibility in the case when the additive is tetraethyllead. At constant level of additive, the octane response depends on the composition of the gasoline; alkanes and cycloalkanes have a greater lead susceptibility than olefins or aromatics. Generally a boost of one road octane number requires the addition of 0.1 g PbEt₄/gallon.

The environmental Protection Agency of the USA issued in the 1970's and 1980's directives for phasing down tetraalkyllead additives in gasoline. Together with the market demands this has caused the tetraalkyllead level to drop in the USA from 1.1 g/gallon to 0.1 g/gallon in the period from 1982 till 1988. Europe is following the trend. These marked

reductions in the use of lead additives will have an impact on many aspects of ecology, health, and industry. It should be mentioned that metallic sodium was produced practically exclusively for synthesizing tetraalkyllead derivatives, till the advent of breeder nuclear reactors.

As an alternative to tetraethyllead or tetramethyllead, one may use methylcyclopentadienyl manganese tricarbonyl but this additive is more expensive.

Gasoline composition differs appreciably according to its manufacture and refinement. Straight-run gasoline has almost equal amounts of paraffins, isoparaffins, naphthenes and aromatics; the cracking procedure introduces appreciable amounts of alkenes (olefins) enhancing thereby the octane rating; catalytic cracking on zeolite catalysts also increases the contents in aromatics which further raises the antiknock ability². On the other hand, the catalytic reforming leads to a gasoline which is devoid of naphthenes and alkenes but is very rich in aromatics. Fluid catalytic cracking was developed in the nineteen forties and fifties, and consists in treating oil vapors with microspheroidal catalyst particles in a fluidized bed at 460 – 530°C; the catalyst is regenerated in a separate reactor by oxidizing the deposited coke with air at 590 – 760°C. Low-molecular alkenes are side-products: propene and the four butenes (1-butene, cis + trans-2-butene, isobutene). These alkenes can be processed for dimerization ($2 C_3H_6 \rightarrow$ isohexane with PON 89), catalytic polymerization yielding "polymer gasoline" with PON 88, or alkylation (the typical PON for an "alkylate" obtained from propene and isobutane is 93).

Octane numbers which will be presented in Tables 2 and 3 for cis/trans stereoisomers of cycloalkanes and alkenes are arithmetic averages; with the three

exceptions mentioned below, octane numbers for such stereoisomers differ by less than 2 units. The exceptions are 2,5-dimethyl-3-hexene (4 units), 1,3-dimethylcyclohexane (4-6 units for RON and MON, respectively), and 1,3,5-trimethylcyclohexane (9-13 units for RON and MON, respectively).

Topological correlations between octane numbers and chemical structure of hydrocarbons

The previously published correlations^{3,4} were uni- or bi-parametric, employed topological indexes with low discriminating ability (i.e. high degeneracy), and had a database of MON and RON octane numbers for only 34 alkanes $C_4 - C_8$. With the centric index ⁵ B, a correlation coefficient $r^2 = 0.893$ and a standard deviation $r = 8.97$ were obtained for the combined series of heptanes and octanes in single-parameter correlations; with the number of carbon atoms N in the alkane as a second parameter, for the series of 34 alkanes $C_4 - C_8$, correlations with $r^2 = 0.723$ ($s = 13.9$) or $r^2 = 0.740$ ($s = 13.4$) were obtained with the centric indices⁵ B and C, respectively. For the separate correlations involving the subsets of heptane or octane isomers, correlations with B and C had $r = 0.988$ and $s = 4.9$. With other topological indices (Hosoya's Z, Randic's $^1\chi$, Wiener's w or the Zagreb Group's M_1)⁶, less satisfactory monoparametric correlations were obtained (and with N as a second parameter, this was also true of biparametric correlations).³ These indexes have been evaluated by Randic⁷ and new descriptors (P'/P and A'/A) have been used to predict the octane numbers of octane isomers.

In a second publication,⁴ for the same set of 34 alkanes $C_4 - C_8$, better uniparametric correlations between MON and the mean square distance were found: $r^2 = 0.90$ and 0.94 , respectively.

In the present paper we have let the SAS package choose via the principal component analysis how many mutually independent variables, and which ones, should be selected for optimizing the correlation. The menu among which the variables were to be chosen included structural indexes such as number N of carbon atoms, and the number T_{Me} of terminal methyl groups.

A comprehensive set of topological indexes was tested; it included molecular connectivity indexes (Randic's ${}^1\chi$ ⁸, Kier and Hall's extended connectivities ${}^2\chi$, ${}^3\chi$, 9,10 and valence chi^{9,10} indexes ${}^o\chi^v$, ${}^1\chi^v$, ${}^v\chi^3$), shape indexes (Balaban's average distance sum connectivity J, ^{11,12,13}, Kier's Kappa indexes,^{14,15} Kier and Hall's Kappa-alpha indexes¹⁶) ($K\alpha$). In addition, chi indexes for path-cluster ${}^4\chi_{pc}$, differences between χ and χ^v indexes ($D^1\chi = {}^1\chi - {}^v\chi^1$), ETS1-ETS3^{17,18} indexes, the sum of the absolute value of the difference between the intrinsic states of the atoms in a molecule ($SUMDELI = \sum_n di$, where n = number of nonhydrogen atoms in the molecule); the molecule flexibility index ($\phi = K\alpha_1 \cdot K\alpha_2/N$, where N = number of non-hydrogen atoms in a molecule), and X_{12} ($X_{12} = {}^1X - {}^2X$) were included.

We used the SAS package,¹⁹ and the MOLCONN program²⁰ for correlations and the calculation of topological indexes.

Correlations for alkanes

A database of 45 alkanes with octane numbers slightly different from those used in the previous publications was available,¹ as shown below.

A three-parameter correlation gave $r^2 = 0.9240$, $s = 8.17$, $F = 166$.

$$(1) \text{ PON} = 146.46(\pm 5.7) - 65.18(\pm 3.8){}^1\chi + 19.65(\pm 3.5)\chi^{12} + 122.96(\pm 7.5) \text{ SUMDELI.}$$

It can be seen from Table 2 that only n-octane is a serious outlier.

A slightly inferior correlation ($r^2 = 0.900$, $s = 9.38$, $F = 123$) was obtained with χ^{12} , ϕ and T_{Me} as independent variables; in this case, propane was the most serious outlier followed by the other n-alkanes.

Correlations for cycloalkanes

A set of 35 cycloalkanes with negligible angle strain (no ring smaller than five-membered) and known octane numbers was tested similarly. So far, to our knowledge, no correlations in this class have been carried out. The best correlation is the following:

$$(2) \text{ PON} = 182.68(\pm 18.9) - 43.61(9.0)^1\chi + 32.61(\pm 4.7)\chi_{PC4} + 13.13(\pm 8.7)K_3,$$

$$r^2 = 0.780, s = 10.8, F = 36.6.$$

It had been known that χ_{PC4} is a good index for cyclic systems.

Results presented in Table 3 indicate one serious outlier, t-butylcyclohexane.

Correlations for alkenes

A large set of 73 alkenes with known octane numbers was investigated as in the preceding cases. Also in this case no previous correlations in this class of compounds appear to have been carried out earlier.

In this case tri-, tetra- and penta-parametric correlations with PON were tested.

A triparametric equation with poor $r^2 = 0.5818$ ($s = 7.75$, $F = 32$) in terms of ${}^o\chi$, ${}^o\chi^v$ and SUMDELI had 1-octene as the most serious outlier, followed by ethene and 1-heptene.

Better results were obtained with the tetraparametric correlation:

$$(3) \text{ PON} = 43.46(\pm 10.2) + 9.90(\pm 1.5)ETS3 + 20.18(\pm 8.9)T_{Me} + 10.17(\pm 2.9)^{12}\chi - 9.64(\pm 0.9)N$$

In this case, $r^2 = 0.765$, $s = 5.85$, $F = 55$ and Table 3 indicates 1-octene as the only serious

outlier.

A slightly inferior result was obtained with ${}^1\chi$, ${}^{12}\chi$, T_{Me} and SUMDELI as the four variables: $r^2 = 0.7286$, $s = 6.29$, $F = 46$. Again, 1-octene was the only serious outlier.

One five-parameter correlation will be mentioned: with ${}^{12}\chi$, ${}^o\chi^y$, T_{Me} , $D^1\chi$ and ETS3 one obtains $r^2 = 0.793$, $s = 5.54$, $F = 57$. In this case 1-octene is the only serious outlier.

Concluding remarks

Attempts to merge the datafiles were unrewarding, probably because the oxidation mechanisms involving knocking (therefore the octane numbers) differ: for alkenes, allylic free radicals, without analogies in the other classes of compounds are the primary intermediates. For cycloalkanes, conformational problems appear for the free-radical intermediates; these radicals may be unable to achieve planarity and inter-bond angles of 120° at the sp^2 -hybridized center.

As an example on merging the file of 45 alkanes with that of 73 alkenes, the correlation in terms of ${}^{12}\chi$, ${}^o\chi^y$, TM, ETS1 and SUMDELI yielded $r^2 = 0.7872$, $s = 9.64$, $F = 83$. In this case the outliers are hexane, heptane, 2-methylheptane, and 2,3,4-trimethyl-2-pentane.

One must also emphasize the fact that the octane numbers for alkanes span a larger range than for alkenes and cycloalkanes and are less clustered. This leads to better correlations with chemical structures.

Acknowledgements. Thanks are expressed by one of us (A.T.B.) to sterling Drug Inc. for support. The assistance of B.B. Brown for computer programming was much appreciated.

References

- (1) Phillips Petroleum Company, "Phillips 66 Reference Data for Hydrocarbons and Petro-Sulfur Compounds," Bulletin No. 521, 1962 (revised 1974).
- (2) J. Scherzer, "Octane-Enhancing Zeolitic FCC Catalysts," Marcel Dekker, New York, 1990.
- (3) A.T. Balaban and I. Motoc, Math. Chem. 1979, 5, 197.
- (4) A.T. Balaban, Pure Appl. Chem., 55, 199 (1983).
- (5) A.T. Balaban, Theor. Chem. Acta, 53, 355 (1979).
- (6) A.T. Balaban, I. Motoc, D. Bonchev and O. Mekenyan, Top Curr. Chem., 1983, 114, 21.
- (7) M. Randic, J. Math. Chem. 1991, 7, 155-168.
- (8) M. Randic, J. Amer. Chem. Soc. 1975, 97, 6609.
- (9) L. B. Kier, L. H. Hall, "Molecular Connectivity in Chemistry and Drug Research", Academic Press, New York, 1976.
- (10) L. B. Kier, L. H. Hall, "Molecular Connectivity in Structure-Activity Analysis", Research Studies Press and Wiley, New York, 1986.
- (11) A. T. Balaban, Chem. Phys. Lett., 1982, 80, 399.
- (12) A. T. Balaban, Pure Appl. Chem., 1983, 55, 199.
- (13) A. T. Balaban, Math. Chem., 1986, 21, 115.
- (14) L. B. Kier, Quant. Struct. Act. Relat., 1985, 4, 109.
- (15) L. B. Kier, Med. Res. Revs., 1987, 7, 417.
- (16) L. B. Kier, Quant. Struct. Act. Relat., 1986, 5, 7.
- (17) L. B. Kier, L. H. Hall, Pharm. Res., 1990, 7, 801.
- (18) L. H. Hall, B. Mohney, L. B. Kier, J. Chem. Inf. Comput. Sci., 1991, 31, 76.
- (19) SAS Institute Inc., "SAS User's Guide: statistics, Version 5 Ed." Cary, NC, 1985.
- (20) The programs MOLCONN and MOLCONN2 can be obtained from Prof. L.H. Hall, Hall Associates Consulting, 2 Davis Street, Quincy, MA 02170.

TABLE 2

MON, RON and PON Values for the alkanes along with the PON values calculated (CALC) using equation 1 and the corresponding residuals (RES).

OBS	NAME	MON	RON	PON	CALC	RES
1	Ethane	99.0	114.9	106.95	100.9	6.0
2	Propane	96.6	111.0	103.80	98.9	4.9
3	Butane	89.1	94.0	91.55	84.1	7.5
4	2-Methylpropane	97.0	102.1	99.55	95.0	4.5
5	Pentane	63.2	61.8	62.50	62.0	0.5
6	2-Methylbutane	89.7	93.0	91.35	91.9	-0.6
7	2,2-Dimethylpropane	80.2	85.5	82.85	88.7	-5.8
8	Hexane	26.0	24.8	25.40	37.2	-11.8
9	3-Methylpentane	73.3	74.5	73.90	81.9	-8.0
10	2-Methylpentane	73.5	73.4	73.45	74.5	-1.0
11	2,3-Dimethylbutane	94.2	104.3	99.25	95.6	3.6
12	2,2-Dimethylbutane	93.4	91.8	92.60	95.6	-3.0
13	Heptane	0.0	0.0	0.00	10.9	-10.9
14	3-Ethylpentane	69.3	65.0	67.15	64.9	2.3
15	3-Methylhexane	55.0	52.0	53.50	61.7	-8.2
16	2-Methylhexane	46.4	42.4	44.40	53.0	-8.6
17	2,3-Dimethylpentane	88.5	91.1	89.80	90.3	-0.5
18	2,4-Dimethylpentane	83.8	83.1	83.45	84.7	-1.3
19	3,3-Dimethylpentane	86.6	80.8	83.70	95.6	-11.9
20	2,2-Dimethylpentane	95.6	92.8	94.20	82.3	11.9
21	2,2,3-Trimethylbutane	101.3	112.1	106.70	103.8	2.9
22	Octane	0.0	0.0	0.00	-16.3	16.3
23	3-Ethylhexane	52.4	33.5	42.95	41.9	1.0
24	3-Methylheptane	35.0	26.8	30.90	38.7	-7.8
25	4-Methylheptane	39.0	26.7	32.85	40.0	-7.1
26	2-Methylheptane	23.8	21.7	22.75	29.0	-6.2
27	3,4-Dimethylhexane	81.7	76.3	79.00	82.1	-3.1
28	2-Methyl-3-ethylpentane	88.1	87.3	87.70	78.0	9.7
29	3-Methyl-3-ethylpentane	88.7	80.8	84.75	88.9	-4.1
30	2,3-Dimethylhexane	78.9	71.3	75.10	73.4	1.7
31	2,4-Dimethylhexane	69.9	65.2	67.55	75.2	-7.7
32	2,5-Dimethylhexane	55.7	55.5	55.60	67.8	-12.2
33	3,3-Dimethylhexane	83.4	75.5	79.45	79.6	-0.1
34	2,2-Dimethylhexane	77.4	72.5	74.95	63.6	11.3
35	2,3,4-Trimethylpentane	95.9	102.7	99.30	96.5	2.8
36	2,3,3-Trimethylpentane	99.4	106.1	102.75	108.6	-5.9
37	2,2,3-Trimethylpentane	99.9	109.6	104.75	102.6	2.1
38	2,2,4-Trimethylpentane	100.0	100.0	100.00	94.3	5.7
39	3,3-Diethylpentane	91.6	84.0	87.80	75.3	12.5
40	2,4-Dimethyl-3-ethylpentane	96.6	105.3	100.95	88.9	12.1
41	2,2-Dimethylheptane	60.5	50.3	55.40	41.6	13.8
42	2,2-Dimethyl-3-ethylpentane	99.5	112.1	105.80	94.6	11.2
43	2,2,3,3-Tetramethylpentane	95.0	116.8	105.90	118.9	-13.0
44	3,3,5-Trimethylheptane	88.7	86.4	87.55	86.7	0.8
45	2,2,3,3-Tetramethylhexane	92.4	112.8	102.60	109.0	-6.4

TABLE 3

MON, RON and PON Values for the cycloalkanes along with the PON values calculated (CALC) using equation 2 and the corresponding residuals (RES).

OBS	NAME	MON	RON	PON	CALC	RES
1	CYCLOPENTANE	84.9	101.6	93.25	82.1	11.2
2	METHYLCYCLOPENTANE	81.0	89.3	85.15	82.7	2.5
3	ETHYLCYCLOPENTANE	61.2	67.2	64.20	64.6	-0.4
4	1,1-DIMETHYLCYCLOPENTANE	89.3	92.3	90.80	97.7	-6.9
5	1,3-DIMETHYLCYCLOPENTANE	72.9	79.9	76.40	79.0	-2.6
6	PROPYLCYCLOPENTANE	28.1	31.2	29.65	49.0	-19.3
7	ISOPROPYLCYCLOPENTANE	76.2	81.1	78.65	70.2	8.4
8	1-ETHYL-3-METHYLCYCLOPENTANE	59.8	57.6	58.70	62.7	-4.0
9	1,1,3-TRIMETHYLCYCLOPENTANE	83.5	81.7	82.60	92.3	-9.7
10	1,2,4-TRIMETHYLCYCLOPENTANE	79.5	89.2	84.35	83.8	0.6
11	ISOBUTYLCYCLOPENTANE	28.2	33.4	30.80	47.9	-17.1
12	1,1,2,4-TETRAMETHYLCYCLOPENTANE	88.0	96.2	92.10	109.2	-17.1
13	CYCLOHEXANE	77.6	84.0	80.80	69.4	11.4
14	METHYLCYCLOHEXANE	73.8	73.8	73.80	67.7	6.1
15	ETHYLCYCLOHEXANE	40.8	46.5	43.65	50.9	-7.3
16	1,1-DIMETHYLCYCLOHEXANE	85.9	87.3	86.60	84.0	2.6
17	1,2-DIMETHYLCYCLOHEXANE	78.7	80.9	79.80	73.4	6.4
18	1,3-DIMETHYLCYCLOHEXANE	67.6	69.3	68.45	65.3	3.1
19	1,4-DIMETHYLCYCLOHEXANE	64.2	67.7	65.95	67.8	-1.8
20	PROPYLCYCLOHEXANE	14.0	17.8	15.90	34.8	-18.9
21	ISOPROPYLCYCLOHEXANE	61.1	62.8	61.95	55.1	6.8
22	1-ETHYL-1-METHYLCYCLOHEXANE	76.7	68.7	72.70	72.2	0.5
23	1,1,2-TRIMETHYLCYCLOHEXANE	87.7	95.7	91.70	101.0	-9.3
24	1,1,3-TRIMETHYLCYCLOHEXANE	82.6	81.3	81.95	77.2	4.7
25	1,2,3-TRIMETHYLCYCLOHEXANE	81.8	84.8	83.30	74.7	8.6
26	1,2,4-TRIMETHYLCYCLOHEXANE	74.3	72.9	73.60	70.2	3.4
27	1,3,5-TRIMETHYLCYCLOHEXANE	63.3	63.8	63.55	59.2	4.4
28	ISOBUTYLCYCLOHEXANE	28.9	33.7	31.30	35.7	-4.4
29	SEC-BUTYLCYCLOHEXANE	55.2	51.0	53.10	37.0	16.1
30	TERT-BUTYLCYCLOHEXANE	89.2	98.5	93.85	72.6	21.3
31	PARA-CYMENE	60.5	67.3	63.90	55.0	8.9
32	1-METHYL-2-PROPYLCYCLOHEXANE	38.8	29.9	34.35	34.8	-0.4
33	CYCLOHEPTANE	40.8	38.9	39.85	55.8	-15.9
34	ETHYLCYCLOHEPTANE	30.0	28.0	29.00	36.7	-7.7
35	CYCLOOCTANE	51.2	71.0	61.10	45.2	15.9

TABLE 14

MON, RON and PON Values for the alkenes along with the PON values calculated (CALC) using equation 3 and the corresponding residuals (RES).

Obs	NAME	MON	RON	PON	CALC	RES
1	ETHENE	75.6	97.3	86.45	93.8	-7.3
2	PROPENE	84.9	101.8	93.35	92.5	0.8
3	1-BUTENE	79.9	98.8	89.35	87.5	1.9
4	2-BUTENE	99.9	101.6	100.75	94.2	6.6
5	2-METHYLPROPENE	90.3	106.3	98.30	97.0	1.3
6	1-PENTENE	77.1	87.9	82.50	80.5	2.0
7	2-PENTENE	87.8	87.8	87.80	87.9	-0.1
8	2-METHYL-1-BUTENE	81.9	98.3	90.10	89.1	1.0
9	3-METHYL-1-BUTENE	97.5	97.5	97.50	94.6	2.9
10	2-METHYL-2-BUTENE	84.7	97.3	91.00	94.8	-3.8
11	1-HEXENE	63.4	76.4	69.90	73.1	-3.2
12	2-HEXENE	80.8	92.7	86.75	80.5	6.2
13	3-HEXENE	80.1	94.0	87.05	81.4	5.6
14	2-METHYL-1-PENTENE	81.5	94.2	87.85	81.8	6.1
15	3-METHYL-1-PENTENE	81.2	96.0	88.60	90.4	-1.8
16	4-METHYL-1-PENTENE	80.9	95.7	88.30	86.9	1.4
17	2-METHYL-2-PENTENE	83.0	97.8	90.40	87.0	3.4
18	3-METHYL-2-PENTENE	81.0	97.2	89.10	90.9	-1.8
19	4-METHYL-2-PENTENE	85.1	98.9	92.00	94.1	-2.1
20	2-ETHYL-1-BUTENE	84.3	99.3	91.80	85.8	6.0
21	2,3-DIMETHYL-1-BUTENE	82.8	101.3	92.05	97.3	-5.3
22	3,3-DIMETHYL-1-BUTENE	93.3	111.7	102.50	97.7	4.8
23	2,3-DIMETHYL-2-BUTENE	80.5	97.4	88.95	96.2	-7.3
24	1-HEPTENE	50.7	54.5	52.60	65.5	-12.9
25	2-HEPTENE	68.8	73.4	71.10	72.8	-1.7
26	3-HEPTENE	79.3	90.0	84.65	74.2	10.5
27	2-METHYL-1-HEXENE	78.8	90.7	84.75	74.3	10.4
28	3-METHYL-1-HEXENE	71.5	82.2	76.85	82.8	-6.0
29	4-METHYL-1-HEXENE	74.0	86.4	80.20	82.3	-2.1
30	5-METHYL-1-HEXENE	64.0	75.5	69.75	79.3	-9.5
31	2-METHYL-2-HEXENE	78.9	90.4	84.65	80.5	4.1
32	3-METHYL-2-HEXENE	79.8	92.0	85.90	83.1	2.8
33	4-METHYL-2-HEXENE	83.0	97.6	90.30	89.6	0.7
34	5-METHYL-2-HEXENE	81.2	94.3	87.75	86.6	1.2
35	2-METHYL-3-HEXENE	82.0	97.9	89.95	87.8	2.2
36	3-METHYL-3-HEXENE	81.4	96.2	88.80	84.0	4.8
37	3-ETHYL-1-PENTENE	81.6	95.6	88.60	85.8	2.8
38	2,3-DIMETHYL-1-PENTENE	84.2	99.3	91.75	92.8	-1.1
39	2,4-DIMETHYL-1-PENTENE	84.6	99.2	91.90	88.0	3.9
40	3,3-DIMETHYL-1-PENTENE	86.1	103.5	94.80	95.4	-0.6
41	3,4-DIMETHYL-1-PENTENE	80.9	98.9	89.90	98.3	-8.4
42	4,4-DIMETHYL-1-PENTENE	85.4	104.4	94.90	89.5	5.4
43	3-ETHYL-2-PENTENE	80.6	93.7	87.15	86.4	0.7
44	2,3-DIMETHYL-2-PENTENE	80.0	97.5	88.75	91.7	-3.0
45	2,4-DIMETHYL-2-PENTENE	84.6	100.0	92.30	94.0	-1.7

TABLE 4. (CONTINUED)

OBS	NAME	MON	RON	PON	CALC	RES
46	3,4-DIMETHYL-2-PENTENE	82.2	96.0	89.10	98.3	-9.2
47	4,4-DIMETHYL-2-PENTENE	90.6	105.3	97.95	96.4	1.5
48	2-ETHYL-3-METHYL-1-BUTENE	82.0	97.0	89.50	93.8	-4.3
49	2,3,3-TRIMETHYL-1-BUTENE	90.5	105.3	97.90	101.0	-3.1
50	1-OCTENE	34.7	28.7	31.70	49.9	-18.2
51	2-OCTENE	56.5	56.3	56.40	65.0	-8.6
52	3-OCTENE	68.1	72.5	70.30	66.5	3.8
53	4-OCTENE	74.3	73.3	73.80	66.9	6.9
54	2-METHYL-1-HEPTENE	66.3	70.2	68.25	66.7	1.6
55	6-METHYL-1-HEPTENE	62.6	63.8	63.20	71.6	-8.4
56	2-METHYL-2-HEPTENE	73.1	79.8	76.45	72.9	3.6
57	6-METHYL-2-HEPTENE	65.5	71.3	68.40	78.7	-10.3
58	2-METHYL-3-HEPTENE	80.6	94.6	87.60	80.4	7.2
59	6-METHYL-3-HEPTENE	82.0	91.3	86.65	80.1	6.5
60	2,3-DIMETHYL-1-HEXENE	83.6	96.3	89.95	85.0	5.0
61	2,3-DIMETHYL-2-HEXENE	79.3	93.1	86.20	83.9	2.3
62	2,5-DIMETHYL-2-HEXENE	82.2	95.2	88.70	86.5	2.2
63	2,2-DIMETHYL-3-HEXENE	88.5	106.0	97.25	90.1	7.2
64	2,5-DIMETHYL-3-HEXENE	85.4	101.9	93.65	94.1	-0.4
65	3-ETHYL-2-METHYL-1-PENTENE	85.3	99.5	92.40	87.8	4.6
66	2,3,3-TRIMETHYL-1-PENTENE	85.7	106.0	95.85	98.4	-2.6
67	2,4,4-TRIMETHYL-1-PENTENE	86.5	106.0	96.25	90.2	6.0
68	2,4,4-TRIMETHYL-2-PENTENE	85.6	102.0	93.80	96.0	-2.2
69	3-ETHYL-2-METHYL-2-PENTENE	82.0	95.6	88.80	86.9	1.9
70	2,3,4-TRIMETHYL-2-PENTENE	80.9	96.6	88.75	98.9	-10.1
71	2,4,4-TRIMETHYL-2-PENTENE	86.2	103.5	94.85	96.0	-1.2
72	3,4,4-TRIMETHYL-2-PENTENE	86.1	103.0	94.55	101.2	-6.7
73	4,4-DIETHYL-1-HEPTENE	74.8	79.8	77.30	71.9	5.4