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ODREĐIVANJE OKTANSKOG BROJA FCC BENZINA PLINSKOM KROMATOGRAFIJOM

Sažetak

Benzin iz procesa fluid katalitičkog krekinga (FCC) pripada grupi benzina s visokim sadržajem nezasićenih ugljikovodika. Zbog njegovog velikog značaja pri namješavanju komercijalnih motornih benzina, vrlo je interesantan za istraživanje korelacija sastava s fizikalno-kemijskim svojstvima, posebice s oktanskim brojem.

U ovom radu koristili smo plinsku kromatografiju visokog razlučivanja za separaciju više od 350 komponenata sadržanih u FCC benzinu. Pri odabiru ulaznih parametara za regresijsku analizu velika količina nezasićenih ugljikovodika predstavljala je specifičan problem zbog znatnog broja nerazlučenih ili loše razlučenih pikova.

U radu je predstavljen novi pristup odabiru ulaznih parametara za postavljanje korelacije kemijskog sastava i istraživačkog oktanskog broja FCC benzina. Postupak uključuje dva stupnja odabira i grupiranja odijeljenih komponenata koji se osniva na faktorima koji imaju najveći utjecaj na istraživački oktanski broj.

UVOD

Istraživački oktanski broj (IOB) jedna je od najznačajnijih empirijskih karakteristika benzina i benzinskih frakcija, te jedan od osnovnih pokazatelja njihove kvalitete. Određuje se prema standardnoj ASTM metodi (1), a dobiveni IOB ukazuje na sklonost ispitivanog benzina ili benzinske frakcije na lupanje.

Kada se provode primjenska istraživanja, čest je problem količina raspoloživog uzorka za analizu kao i dostupnost CFR motora. Zbog toga je interes usmjeren na određivanje IOB-a na osnovi kemijskog sastava pomoću raznih analitičkih tehnika. Tako dobiveni podaci o kemijskom sastavu koreliraju se s IOB-om određenim

eksperimentalno i primjenjuju kao nestandardne metode koje se upotrebljavaju najčešće u praćenju istraživanja koja se rade u manjem mjerilu.

Do sada su objavljeni radovi koji opisuju određivanje IOB na osnovi kemijskog sastava dobivenog iz analiza plinskom kromatografijom (2-5), NMR (6-9) i IR (10) spektrometrijom. Radovi koji se odnose na određivanje IOB na osnovi plinsko-kromatografskih podataka osnivaju se na selektiranju odijeljenih ugljikovodika u grupe koje nužno ne slijede jedan od pet tipova ugljikovodika zastupljenih u uzorku benzina.

A.Haas i suradnici (3) podijelili su benzin iz procesa fluid-katalitičkog krekinga (FCC benzin) na 19 frakcija slijedom vrelišta, te proučavali odnos grupnog sastava svake pojedine frakcije i IOB određenog na CFR motoru. C. Anderson i suradnici (2) podijelili su motorni benzin i benzin iz procesa katalitičkog reforminga na 31 grupu ugljikovodika slijedom eluiranja, s time da su obuhvatili sve komponente sadržane u navedenim benzinima. G. Protić-Lovašić i suradnici (4) postavili su korelaciju strukturnog sastava i IOB benzina iz procesa katalitičkog reforminga na osnovi određenog grupnog sastava s time da su iz n-parafinske i izoparafinske skupine izdvojili pojedine ugljikovodike i uvrstili ih kao zasebne varijable u regresijsku analizu.

U radu je modificiran način grupiranja ugljikovodika u svrhu pronalaženja optimalne korelacije s IOB primijenjen na benzin iz procesa fluid-katalitičkog krekinga (FCC). Podaci o sastavu dobiveni su na osnovi analiza plinskom kromatografijom visokog razlučivanja. FCC benzin interesantan je zbog visokog IOB-a koji posjeduje te je kao takav zastupljen kao komponenta za namješavanje motornog benzina.

EKSPERIMENTALNI DIO

Uzorci benzina

Uzorci benzina iz procesa fluid-katalitičkog krekinga dobiveni su iz INA Rafinerija nafte Rijeka, gdje je i određen oktanski broj na CFR motoru metodom ASTM 2699 (1). Raspon vrijednosti oktanskih brojeva dobivenih uzoraka benzina je od 91.0 do 93.5.

Aparatura i radni uvjeti

Plinski kromatograf CARLO ERBA 2900 Series, Capillary GC s kriogenom jedinicom. Injektor sa i bez cijepanja uzorka izvedbe po Grobu. Detektor plamenoionizacijski.

Kapilarna kolona fused silica SPB-1, Supelco, 0.32 mm, debljina filma 1.0 μm, duljina 60 m. Plin nosilac vodik, protok kroz kolonu t_{CH4}= 210 s. Protok na spliteru 40 ml/min. Količina uzorka 0.2 μl.

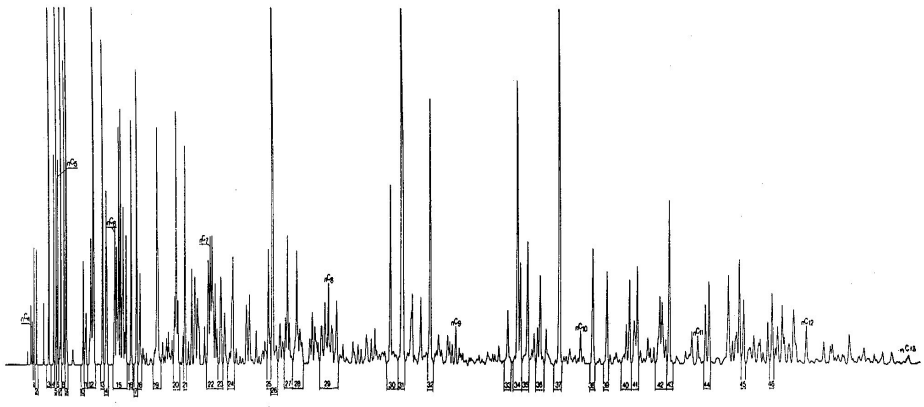
Temperatura injektora 220^{o}C, temeratura detektora 250^{o}C. Temperatura kolone od 20^{o}C do 220^{o}C, linearno zagrijavanje od 2^{o}/min.

REZULTATI I DISKUSIJA

Određivanje strukture i tipa ugljikovodika sadržanih u FCC benzinu provedeno je na osnovi interne metode koja se osniva na podacima o vremenu zadržavanja čistog spoja (Kovátsevi indeksi), podacima iz masenih spektara dobivenih vezanim sustavom plinska kromatografija-spektrometrija masa, podacima dobivenih tekućinskom kromatografijom (FIA), te podacima dobivenim na osnovi bromiranja olefinske frakcije benzina. Tipičan kromatogram FCC benzina prikazan je na slici 1.

Slika 1: Kromatogram FCC benzina sa označenim grupama ugljikovodika

Figure 1: FCC gasoline chromatogram with marked hydrocarbon groups



U svrhu postavljanja korelacije sastava FCC benzina s IOB, komponente odijeljene u FCC benzinu plinskom kromatografijom podijeljene su u 46 grupa (tablica 1, slika 1), kojima je obuhvaćeno, ovisno o uzorku, prosječno 70 do 80 mas.% uzorka. Težište odabira grupa osniva se na činjenici da olefinski i aromatski ugljikovodici najviše utječu na IOB FCC benzina, dok oni izoparafinski, koji su vrlo značajni kod postavljanja korelacije sastava i IOB motornih benzina, ovdje ne igraju presudnu ulogu (9).

Također su uzeti u obzir pikovi čija je zastupljenost znatna, odnosno iznosi i do nekoliko masenih postotaka uzorka (npr. nC_5, $3MeC_5$, $MeCyC_5$, $3MeC_6$), što je u višekomponentnoj smjesi kakva je FCC benzin vrlo značajno. Uzete su u obzir i grupe olefina koji pojedinačno nisu znatnije zastupljeni (grupe 15, 22, 29), ali su bliskim vremenima zadržavanja grupirani u pravilnim razmacima oko n-parafina (npr. n-heksan, n-oktan), te skupno čine znatniji postotak tipa ugljikovodika koji, kako je

već spomenuto, znatno utječe na vrijednost IOB FCC benzina. N-parafin je zadržan u skupini jer ga je zbog relativno lošije razlučenosti u tim dijelovima kromatograma teško kvalitetno izdvojiti iz skupine.

Tablica 1: Ugljikovodici grupirani za regresijsku analizu, tip ugljikovodika spojeva sadržanih u grupama i tip ugljikovodika grupe

BR. GRUPE	NAZIVI SPOJEVA	TIP CH	TI CH GRUPE
1	C_4=2 trans	ol	ol
2	C_4=2 cis	ol	ol
3	iC_5	ip	ip
4	C_5=1	ol	ol
5	2MeC_4=1	ol	ol
6	nC_5	np	np
7	ol C_5=2trans	ol ol	ol
8	C_5=2cis; 3,3diMeC_4=1	ol	ol
9	2MeC_4=2 ol	ol ol	ol
10	CyC_5=	ol	ol
11	4MeC_5=1 3MeC_5=1	ol ol	ol
12	CyC_5 2,3diMeC_4 4MeC_5=2trans 2MeC_5	cp ip ol ip	ip
13	3MeC_5	ip	ip
14	2MeC_5=1 C_6=1	ol ol	ol
15	nC_6; (2EtC_4=1) C_6=3trans ol C_6=2trans 2MeC_5=2 ol 3MeC_5=2trans; 4MeCyC_5=1 ol C_6=2cis	np ol ol ol ol ol ol ol ol	ol
16	3,3diMeC_5=1; 3MeC_5=2cis	ol	ol
17	MeCyC_5	cp	cp
18	2,4diMeC_5; (2,3diMeC_4=2) ol	ip ol	ol
19	ol ol 1MeCyC_5=1 Benzen 3MeC_6=1	ol ol ol ar ol	ar

20	ol $2MeC_6$ $2,3diMeC_5$	ol ip ip	ip
21	$3MeC_6$	ip	ip
22	C_7=3trans nC_7; (ol) C_7=3cis C_7=2trans ol	ol np ol ol ol	ol
23	$2,4triMeC_5$=1	ol	ol
24	ol p $MeCyC_6$	ol p cp	cp
25	ol ol	ol ol	ol
26	Toluen ol ol	ar ol ol	ar
27	$1MeCyC_6$=1 $2MeC_7$ $4MeC_7$ $3,4diMeC_6$; (ol)	ol ip ip ip	ip
28	ol ol $3MeC_7$ $1c,2t,3triMeCyC_6$; (ol) $1t,4diMeCyC_6$ p; (CyC_7=)	ol ol ip cp cp p	ip
29	C_8=4trans; ol $1t,2diMeCyC_6$ C_8=3trans nC_8; (C_8=3cis); ($2MeC_7$=2) p C_8=2trans; ($1c,4diMeCyC_6$) ol ol	ol cp ol np p ol ol ol	ol
30	$3MeC_8$=1 Etilbenzen ol $1,2,4triMeCyC_6$trans p; (ol) p; (ol)	ol ar ol cp p p	ar
31	ol; ($1,3,5triMeCyC_6$cis) m-ksilen; p-ksilen	ol ar	ar
32	o-ksilen p	ar p	ar

33	p nPrB p	p ar p	ar
34	p 1Me3EtB 1Me4EtB	p ar ar	ar
35	ol; (p) p 1,3,5triMeB	ol p ar	ar
36	2,3diMeC_8; 2MeC_9 1Me2EtB p; (ol)	ip ar p	ar
37	p; (ol) 1,2,4triMeB	p ar	ar
38	1,2,3triMeB	ar	ar
39	p Indan	p ar	ar
40	p 1,3diEtB 1Me3nPrB	p ar ar	ar
41	1,4diEtB; 1Me4nPrB; nBuB 1,3diMe5EtB	ar ar	ar
42	p 1,4diMe2EtB 1,3diMe4EtB; (p) p	p ar ar p	ar
43	1,2diMe4EtB p	ar p	ar
44	1,2,4,5tetraMeB 1,2,3,5tetraMeB	ar ar	ar
45	1,2,3,4tetraMeB; (ol)	ar	ar
46	Naftalen	ar	ar

Legenda:

np – n-parafin
ip – izoparafin
cp – cikloparafin
ol – olefin
ar – aromat
p – neolefinski ugljikovodik

Me – metilna skupina
Et – etilna skupina
Pr – propilna skupina
i – izo struktura
Cy – ciklo struktura
t – trans
c – cis
B – benzen

Aromatske skupine ugljikovodika nešto je jednostavnije izdvojiti, jer u toj temperaturnoj frakciji FCC benzina izostaje koeluiranje olefinskih ugljikovodika koji zadaju najveće probleme na nižim temperaturama. Iznimka su benzen, toluen i etil-

benzen (grupe 19, 26 i 30) koji su zbog nižeg vrelišta još uvijek okruženi olefinima i od njih loše razlučeni, te je stoga u sva tri slučaja u obzir uzeta cijela okolna skupina pikova. Aromatski ugljikovodici navedeni u grupama 45 i 46 uzeti su u obzir kao predstavnici destilacijskog ostatka frakcije.

Odijeljenih 46 grupa ugljikovodika predstavlja prevelik broj ulaznih varijabli za postavljanje korelacije, te je stoga definiranim grupama pripisan pripadajući tip ugljikovodika ili skupini ugljikovodika koja je u grupi najzastupljenija (tablica 1). Izračunato je da najzastupljeniji tip ugljikovodika u 78 % slučajeva (grupa) iznosi između 90 i 100% grupe, dok se preostalih 22% zastupljenosti kreće između 60 i 80%. Tim postupkom grupe su svrstane u pet skupina – n-parafinsku, izoparafinsku, cikloparafinsku, olefinsku i aromatsku. Njihovim zbrojem (tablica 2) dobiveno je pet nezavisnih varijabli koje ulaze u regresijsku analizu.

Tablica 2: Grupe ugljikovodika razvrstane prema tipu ugljikovodika

TIP UGLJIKOVODIKA	REDNI BROJ GRUPE
n-parafini	6
izoparafini	3, 12, 13, 18, 20, 21, 27, 28
cikloparafini	17, 24
olefini	1, 2, 4, 5, 7, 8, 9, 10, 11, 14, 15, 16, 22, 23, 25, 29
aromati	19, 26, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46

U tablici 3 dani su maseni postoci grupiranih ulaznih varijabli i eksperimentalno dobiveni IOB za 50 FCC benzina na osnovi kojih je korelacija postavljena.

Višestrukoj linearnoj regresijskoj analizi podvrgnute su sve ulazne varijable i njihove međusobne kombinacije, s time da su aromatska i olefinska grupa bile uvijek prisutne zbog svoje visoke pojedinačne oktanske vrijednosti. Preostale tri ulazne varijable kombinirane su da bi se utvrdio njihov doprinos u regresijskoj analizi. Ispitivanja su pokazala da se najbolja korelacija dobiva ukoliko se svih pet ulaznih varijabli uvrsti u regresijsku analizu, te da izostavljanje bilo koje od tri navedene varijable daje lošije rezultate. Rezultati regresijske analize prikazani su u tablici 4.

Opći izraz za izračunavanje IOB prikazan je jednadžbom 1.

$$IOB = \sum_{i=1}^{n} a_i x_i + C \qquad [1]$$

gdje je: a_i – koeficijent za definiranu grupu (i)

x_i – mas.% definirane grupe (i)

C - konstanta

Tablica 3: IOB (EKSPERIM.) i koncentracije ulaznih varijabli u mas.% za 50 benzina na osnovi kojih je postavljena korelacija

REDNI BROJ	IOB EKSPERIM.	NP % m/m	IP % m/m	CP % m/m	OL % m/m	AR % m/m
1	91.5	1.061	19.465	2.531	23.702	29.112
2	91.5	1.000	19.358	2.491	23.070	30.082
3	92.0	0.951	18.470	2.439	22.438	31.355
4	92.0	1.171	21.975	2.778	23.969	28.802
5	91.8	1.077	20.862	2.572	23.028	29.820
6	91.5	1.063	22.161	2.194	21.651	28.875
7	91.5	1.392	26.503	2.271	23.099	23.180
8	91.8	1.055	21.136	2.827	22.617	29.625
9	91.0	1.256	25.094	2.228	22.726	26.338
10	91.3	1.320	26.031	2.285	22.999	25.239
11	92.0	0.965	18.205	2.536	25.157	28.457
12	92.0	1.027	19.542	2.701	26.433	27.681
13	92.0	0.954	19.927	2.742	22.247	29.132
14	92.0	1.064	22.084	2.712	22.453	28.532
15	92.5	0.938	18.315	2.603	24.339	30.417
16	93.0	1.010	19.169	2.720	25.105	28.968
17	93.0	0.838	15.672	2.267	26.757	27.954
18	93.0	0.948	16.827	2.393	29.081	25.237
19	92.5	0.854	15.018	2.193	29.001	26.316
20	92.5	0.831	14.730	2.348	26.658	28.294
21	93.4	0.773	15.649	2.438	25.269	27.599
22	93.5	1.014	17.961	2.438	29.885	24.377
23	93.3	0.880	16.603	2.383	27.643	26.481
24	93.4	0.710	14.183	2.161	23.951	29.094
25	92.0	0.714	15.249	2.503	23.626	30.446
26	92.5	0.808	16.754	2.631	22.251	33.076
27	92.5	0.986	18.025	2.651	25.122	30.641
28	92.0	0.439	15.352	2.870	18.587	34.964
29	92.5	0.406	13.691	2.617	19.969	33.934

30	92.0	1.001	24.188	2.541	18.569	29.763
31	92.0	0.530	14.822	2.702	22.414	31.360
32	92.0	0.463	15.135	2.760	18.901	34.429
33	92.0	0.943	19.584	1.597	23.559	26.070
34	93.2	0.779	15.060	2.281	31.251	25.054
35	92.5	0.243	9.734	1.554	15.726	36.079
36	92.0	0.949	18.443	2.539	26.121	25.077
37	93.0	0.274	13.957	2.818	18.557	34.923
38	92.0	0.842	18.506	2.783	22.894	30.951
39	92.6	0.771	20.004	2.835	18.369	32.756
40	92.8	0.614	16.243	3.064	22.070	33.026
41	92.0	0.734	17.410	2.504	20.294	29.728
42	92.0	0.960	20.065	2.674	23.801	26.358
43	92.0	0.490	11.894	1.737	13.979	31.506
44	92.0	1.027	20.748	2.696	24.618	24.958
45	92.0	0.658	14.201	1.941	16.917	28.775
46	92.5	0.917	16.704	2.412	27.898	26.047
47	92.8	0.891	16.910	2.413	27.022	25.898
48	92.8	0.829	16.712	2.477	25.328	29.325
49	93.0	1.010	18.903	2.554	26.031	26.789
50	93.0	0.943	20.157	2.626	25.922	26.510

Jednadžbom 2 prikazana je regresijska jednadžba za izračunavanje IOB FCC benzina na osnovi sastava dobivenog plinskokromatografskom analizom.

IOB (GC) = -1.5755 **NP* - 0.0189 * *IP* + 0.0909 * *CP* + 0.1088 * *OL* - 0.0203 * *AR* + 91.8309 [2]

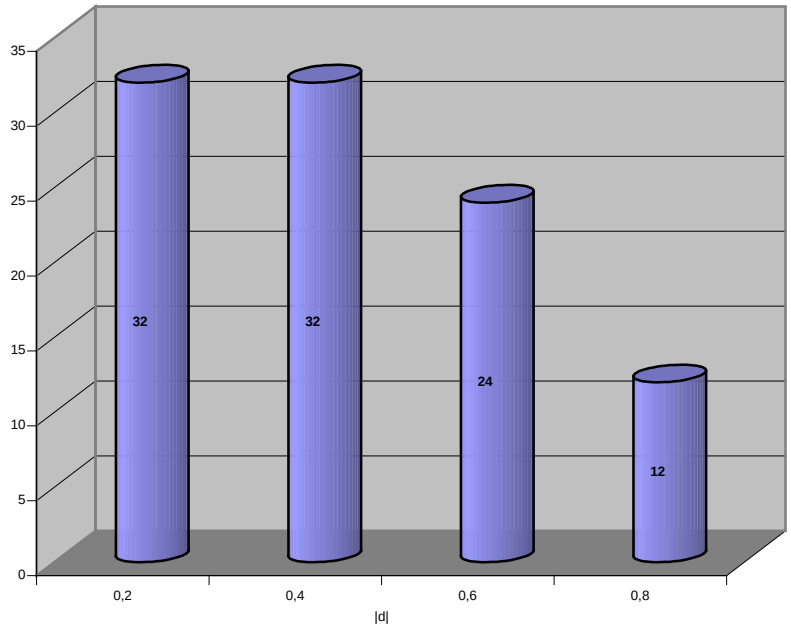
Standardna devijacija (s) izračunata je prema sljedećem izrazu (jednadžba 3).

$$s = \sqrt{\frac{\sum_{i=1}^{n} [RON\ (GC)_i - RON(ASTM)_i]^2}{n-1}} \qquad [3]$$

Odnos IOB određenog eksperimentalno i onog određenog na osnovi rezultata regresijske analize prikazan je na slici 2. Standardna ASTM metoda navodi da je reproducibilnost za 95% ispitivanih uzoraka do 0.6, odnosno 0.7 oktana za vrijednosti IOB od 90, odnosno 95 oktana. Apsolutna vrijednost odstupanja izračunatih vrijednosti IOB u 88% obrađenih uzoraka kreće se u granicama od 0.6 oktana što ukazuje na vrlo dobro slaganje (slika 3).

Ponovljivost određivanja IOB provjerena je na jednom uzorku FCC benzina (ASTM IOB = 92.0) pet puta uz iste eksperimentalne uvjete. Dobivena je srednja vrijednost IOB od 92.10 oktana i standardna devijacija 0.172. Regresijska jednadžba provjerena je na grupi FCC benzina i dobiveno je prosječno odstupanje od 0.25 oktana.

Slika 3: Raspodjela uzoraka po apsolutnim vrijednostima odstupanja



ZAKLJUČAK

U svrhu postavljanja korelacije sastava FCC benzina s IOB, komponente odijeljene u FCC benzinu podijeljene su u 46 grupa kojima je obuhvaćeno 70-80 mas.% uzorka. Definiranim grupama pripisan je pripadajući tip ugljikovodika određen prema ugljikovodiku ili skupini koja je u grupi najzastupljenija. Njihovim zbrojem je dobiveno 5 nezavisnih varijabli koje ulaze u regresijsku analizu.

Linearnom regresijskom analizom dobivena je jednadžba za izračunavanje IOB na osnovi kemijskog sastava. Apsolutna vrijednost odstupanja za 88% obrađenih uzoraka kreće se do 0.6 oktana, a izračunata ponovljivost je 0.172.

Regresijska jednadžba provjerena je na grupi FCC benzina i dobiveno je prosječno odstupanje od 0.25 oktana.

Metoda je razvijena za laboratorijsko praćenje procesa i ne zahtijeva veliku količinu uzorka (0.2µl). Također je pogodna u svakodnevnoj karakterizaciji procesa prerade.

FCC GASOLINE RESEARCH OCTANE NUMBER DETERMINATION BY GAS CHROMATOGRAPHY

Abstract

The FCC gasoline belongs to the group of gasolines with a high content of unsaturated hydrocarbons. Because of its significance as blending component, the correlations connecting composition and physical properties, especially the octane number, are of great significance.

For the separation of more than 350 components, the high-resolution gas chromatography is used. The main problem was the high content of unsaturated hydrocarbons because of a considerable number of unseparated and poorly separated peaks.

For the selection of parameters to be correlated, a new approach has been used. The method includes two steps for selection and grouping of separated components, based on factors with the highest influence on RON.

INTRODUCTION

The research octane number (RON) is one among the most significant empirical properties of gasoline and gasoline fractions, as well as one of the basic indicators of their quality. It is determined according to the standard ASTM method (1), while the obtained RON points to the tested gasoline or gasoline fraction being prone to knocking.

When field tests are being performed, the problem is often the volume of the sample available for analysis, as well as the availability of a CFR engine. That is why the interest is directed towards determining RON based on chemical composition, using various analytical techniques. Thus obtained data on the chemical composition are correlated with RON determined experimentally and applied as non-standard methods used mostly in research done to a smaller scale.

The papers published so far describe RON determination based on chemical composition obtained from the analyses using gas chromatography (2-5), NMR (6-9) and IR (10) spectrometry. The papers referring to RON determination based on gas-chromatographic data are founded on distributting separated hydrocarbons into groups which do not necessarily follow any of the five hydrocarbon types present in the gasoline sample.

A. Haas and associates (3) have distributed FCC gasoline into 19 fractions with regard to the boiling point, and have then studied the relation of the each individual fraction's group composition with the RON determined on the CFR engine. C. Anderson and associates (2) have classified motor gasoline and gasoline from the catalytic reforming process into 31 hydrocarbon groups according to eluation, encompassing all the components contained in the said gasoline in the process. G. Protić-Lovašić and associates (4) have set up a correlation of the structural composition and RON of the catalytic reforming process gasoline based on the group composition set, having isolated certain hydrocarbons from the n-paraffinic and isoparaffinic group and included them as separate variables into the regression analysis.

The paper encompasses a modification of the way of grouping hydrocarbons for the purpose of finding an optimal correlation with RON, applied on FCC gasoline. Data on the composition have been obtained based on high resolution gas chromatography analyses. The FCC gasoline is interesting because of its high RON, as such represented as a motor gasoline blending component.

THE EXPERIMENTAL PART

Gasoline samples

FCC gasoline samples have been obtained from INA's Oil Refinery in Rijeka, where the octane number was also determined on a CFR engine, using the ASTM 2699

method (1). The octane number values of the gasoline samples obtained range from 91.0 to 93.5.

Apparatus and operating conditions

Gas chromatograph CARLO ERBA 2900 Series, Capillary GC with a cryogenic unit. Injector with and without sample splitting according to Grob. Flame ionization detector.

Capillary column fused silica SPB-1, Supelco, 0.32 mm, film thickness 1.0 μm, length 60 m. Carrier gas - hydrogen, flow through the column t_{CH4}= 210 s. Flow at the splitter 40 ml/min. Sample volume 0.2 μl.

Injector temperature 220^{o}C, detector temperature 250^{o}C. Column temperature from 20^{o}C to 220^{o}C, linear heating of 2^{o}/min.

RESULTS AND DISCUSSION

Determination of the structure and type of hydrocarbons contained in the FCC gasoline has been performed using an inhouse method, based on the data on the time of keeping clean compound (Kováts' indices), data from the mass spectra obtained by the connected gas chromatography-mass spectrometry system, data obtained by fluid chromatography (FIA), and data obtained on the basis of bromizing the gasoline olefine fraction. A typical FCC gasoline chromatogram is shown in Figure 1.

For the purpose of correlating the FCC gasoline composition with RON, the components separated in FCC gasoline using gas chromatography have been divided into 46 groups (Table 1, Figure 1), encompassing – depending on the sample – the average of 70 to 80 mass.% of sample. The criterion in choosing groups is based on the fact that olefine and aromatic hydrocarbons have the greatest impact on the RON of the FCC gasoline, while those isoparaffinic, most significant when correlating the composition and RON of motor gasoline, do not play a decisive role here (9). We have also taken into account the highly represented peaks, i.e. those in the amount of up to several mass percents of the sample (e.g. nC_5, $3MeC_5$, $MeCyC_5$, $3MeC_6$), which is most significant for a multicomponent blend such as FCC gasoline. We have also taken into account groups of olefins which are not much represented individually (groups 15, 22, 29), but are closely and regularly grouped around n-paraffins (e.g. n-hexane, n-octane). As a group, they constitute a rather significant percentage of a hydrocarbon type, which, as we have already mentioned, has a considerable impact on the RON value of FCC gasoline. N-paraffin has been kept in the group, because – due to a relatively poor resolution in these parts of the chromatogram – it is difficult to isolate them from the group in a satisfactory manner.

Aromatic groups of hydrocarbons are somewhat easier to isolate, because, this particular temperature fraction of FCC gasoline lacks the co-elution of olefine hydrocarbons causing most trouble at lower temperatures. The exceptions are

benzene, toluene and ethyl-benzene (groups 19, 26 i 30), which are – due to a lower boiling point – still surrounded by olefins and poorely separated from them, which is why in all three cases the entire surrounding group of peaks was taken into account.

Table 1: Hydrocarbons grouped for regression analysis, hydrocarbon type of compounds contained in groups and group hydrocarbon type

GROUP N°	COMPOUND NAME S	CH TYPE	GROUP CH TYPE
1	C_4=2 trans	ol	ol
2	C_4=2 cis	ol	ol
3	iC_5	ip	ip
4	C_5=1	ol	ol
5	$2MeC_4$=1	ol	ol
6	nC_5	np	np
7	ol C_5=2trans	ol ol	ol
8	C_5=2cis; $3,3diMeC_4$=1	ol	ol
9	$2MeC_4$=2 ol	ol ol	ol
10	CyC_5=	ol	ol
11	$4MeC_5$=1 $3MeC_5$=1	ol ol	ol
12	CyC_5 $2,3diMeC_4$ $4MeC_5$=2trans $2MeC_5$	cp ip ol ip	ip
13	$3MeC_5$	ip	ip
14	$2MeC_5$=1 C_6=1	ol ol	ol
15	nC_6; ($2EtC_4$=1) C_6=3trans ol C_6=2trans $2MeC_5$=2 ol $3MeC_5$=2trans; $4MeCyC_5$=1 ol C_6=2cis	np ol ol ol ol ol ol ol ol	ol
16	$3,3diMeC_5$=1; $3MeC_5$=2cis	ol	ol
17	$MeCyC_5$	cp	cp
18	$2,4diMeC_5$; ($2,3diMeC_4$=2) ol	ip ol	ol
19	ol ol $1MeCyC_5$=1 Benzene $3MeC_6$=1	ol ol ol ar ol	ar

20	ol 2MeC$_6$ 2,3diMeC$_5$	ol ip ip	ip
21	3MeC$_6$	ip	ip
22	C$_7$=3trans nC$_7$; (ol) C$_7$=3cis C$_7$=2trans ol	ol np ol ol ol	ol
23	2,4triMeC$_5$=1	ol	ol
24	ol p MeCyC$_6$	ol p cp	cp
25	ol ol	ol ol	ol
26	Toluene ol ol	ar ol ol	ar
27	1MeCyC$_6$=1 2MeC$_7$ 4MeC$_7$ 3,4diMeC$_6$; (ol)	ol ip ip ip	ip
28	ol ol 3MeC$_7$ 1c,2t,3triMeCyC$_6$; (ol) 1t,4diMeCyC$_6$ p; (CyC$_7$=)	ol ol ip cp cp p	ip
29	C$_8$=4trans; ol 1t,2diMeCyC$_6$ C$_8$=3trans nC$_8$; (C$_8$=3cis); (2MeC$_7$=2) p C$_8$=2trans; (1c,4diMeCyC$_6$) ol ol	ol cp ol np p ol ol ol	ol
30	3MeC$_8$=1 Ethylbenzene ol 1,2,4triMeCyC$_6$trans p; (ol) p; (ol)	ol ar ol cp p p	ar
31	ol; (1,3,5triMeCyC$_6$cis) m-xylene; p-xylene	ol ar	ar
32	o-xylene p	ar p	ar

33	p nPrB p	p ar p	ar
34	p 1Me3EtB 1Me4EtB	p ar ar	ar
35	ol; (p) p 1,3,5triMeB	ol p ar	ar
36	2,3diMeC_8; 2MeC_9 1Me2EtB p; (ol)	ip ar p	ar
37	p; (ol) 1,2,4triMeB	p ar	ar
38	1,2,3triMeB	ar	ar
39	p Indene	p ar	ar
40	p 1,3diEtB 1Me3nPrB	p ar ar	ar
41	1,4diEtB; 1Me4nPrB; nBuB 1,3diMe5EtB	ar ar	ar
42	p 1,4diMe2EtB 1,3diMe4EtB; (p) p	p ar ar p	ar
43	1,2diMe4EtB p	ar p	ar
44	1,2,4,5tetraMeB 1,2,3,5tetraMeB	ar ar	ar
45	1,2,3,4tetraMeB; (ol)	ar	ar
46	Naphtalene	ar	ar

Key:

np – n-paraffin
ip – isoparaffin
cp – cycloparaffin
ol – olefin
ar – aromatic
p – nonolefinic hydrocarbon

Me – methyl group
Et – ethyl group
Pr – propyl group
i – iso structure
Cy – cyclo structure
t – trans
c – cis
B - benzene

Aromatic hydrocarbons listed in groups 45 and 46 were taken into account as representatives of the fraction distillation residue.

The separated 46 groups of hydrocarbons constitute too high a number of input variables for setting up the correlation, which is why the defined groups have been assigned the accompanying hydrocarbon type or the hydrocarbon complex which is the most represented one (Table 1). It has been calculated that the most represented type of hydrocarbons in 78 % of the cases (groups) encompasses between 90 and 100 % of the group, while in the remaining 22 % the representation level ranges between 60 and 80%. This procedure classifies the groups into five complexes – n-paraffinic, isoparaffinic, cycloparaffinic, olefine and aromatic. Their sum (Table 2) provides five independent variables entering the regression analysis.

Table 2: Groups of hydrocarbons classified per hydrocarbon type

HYDROCA ʁBON TYPE	GROUP NUMBER
n-paraffins	6
isoparaffins	3, 12, 13, 18, 20, 21, 27, 28
cycloparaffins	17, 24
olefins	1, 2, 4, 5, 7, 8, 9, 10, 11, 14, 15, 16, 22, 23, 25, 29
aromatics	19, 26, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46

Table 3 provides mass flows of the grouped input variables and experimentally obtained RONs for 50 FCC gasoline types based on which the correlation has been set up.

All the input variables and their mutual combinations were subjected to a multiple linear regression analysis, with the aromatic and olefin groups always present due to their high individual octane values. The remaining three input variables were combined so as to determine their contribution in the regression analysis. Tests have shown that the best correlation is obtained if all five input variables are included into the regression analysis, and that the leaving out of any of the three mentioned variables yields poorer results. The regression analysis results are shown in Table 4.

The general way of calculating RON is shown in equation 1.

$$IOB = \sum_{i=1}^{n} a_i x_i + C \qquad [1]$$

where: a_i – coefficient for defined group (i)

x_i – mass.% of defined group (i)

C – constant value

Table 3: RON (EXPERIM.) and concentrations of input variables in mass.% for the 50 gasoline types based on which the correlation has been set up

N°	EXPERIM. RON	NP mass.%	IP mass.%	CP mass.%	OL mass.%	AR mass.%
1	91.5	1.061	19.465	2.531	23.702	29.112
2	91.5	1.000	19.358	2.491	23.070	30.082
3	92.0	0.951	18.470	2.439	22.438	31.355
4	92.0	1.171	21.975	2.778	23.969	28.802
5	91.8	1.077	20.862	2.572	23.028	29.820
6	91.5	1.063	22.161	2.194	21.651	28.875
7	91.5	1.392	26.503	2.271	23.099	23.180
8	91.8	1.055	21.136	2.827	22.617	29.625
9	91.0	1.256	25.094	2.228	22.726	26.338
10	91.3	1.320	26.031	2.285	22.999	25.239
11	92.0	0.965	18.205	2.536	25.157	28.457
12	92.0	1.027	19.542	2.701	26.433	27.681
13	92.0	0.954	19.927	2.742	22.247	29.132
14	92.0	1.064	22.084	2.712	22.453	28.532
15	92.5	0.938	18.315	2.603	24.339	30.417
16	93.0	1.010	19.169	2.720	25.105	28.968
17	93.0	0.838	15.672	2.267	26.757	27.954
18	93.0	0.948	16.827	2.393	29.081	25.237
19	92.5	0.854	15.018	2.193	29.001	26.316
20	92.5	0.831	14.730	2.348	26.658	28.294
21	93.4	0.773	15.649	2.438	25.269	27.599
22	93.5	1.014	17.961	2.438	29.885	24.377
23	93.3	0.880	16.603	2.383	27.643	26.481
24	93.4	0.710	14.183	2.161	23.951	29.094
25	92.0	0.714	15.249	2.503	23.626	30.446
26	92.5	0.808	16.754	2.631	22.251	33.076
27	92.5	0.986	18.025	2.651	25.122	30.641
28	92.0	0.439	15.352	2.870	18.587	34.964
29	92.5	0.406	13.691	2.617	19.969	33.934
30	92.0	1.001	24.188	2.541	18.569	29.763
31	92.0	0.530	14.822	2.702	22.414	31.360
32	92.0	0.463	15.135	2.760	18.901	34.429
33	92.0	0.943	19.584	1.597	23.559	26.070
34	93.2	0.779	15.060	2.281	31.251	25.054
35	92.5	0.243	9.734	1.554	15.726	36.079
36	92.0	0.949	18.443	2.539	26.121	25.077
37	93.0	0.274	13.957	2.818	18.557	34.923

38	92.0	0.842	18.506	2.783	22.894	30.951
39	92.6	0.771	20.004	2.835	18.369	32.756
40	92.8	0.614	16.243	3.064	22.070	33.026
41	92.0	0.734	17.410	2.504	20.294	29.728
42	92.0	0.960	20.065	2.674	23.801	26.358
43	92.0	0.490	11.894	1.737	13.979	31.506
44	92.0	1.027	20.748	2.696	24.618	24.958
45	92.0	0.658	14.201	1.941	16.917	28.775
46	92.5	0.917	16.704	2.412	27.898	26.047
47	92.8	0.891	16.910	2.413	27.022	25.898
48	92.8	0.829	16.712	2.477	25.328	29.325
49	93.0	1.010	18.903	2.554	26.031	26.789
50	93.0	0.943	20.157	2.626	25.922	26.510

Equation 2 shows the regression equation for calculating the RON of FCC gasoline based on the composition obtained through gas chromatographic analysis.

IOB (GC) = -1.5755 **NP* - 0.0189 * *IP* + 0.0909 * *CP* + 0.1088 * *OL* - 0.0203 * *AR* + 91.8309 [2]

Standard deviation (s) has been calculated as follows (equation 3).

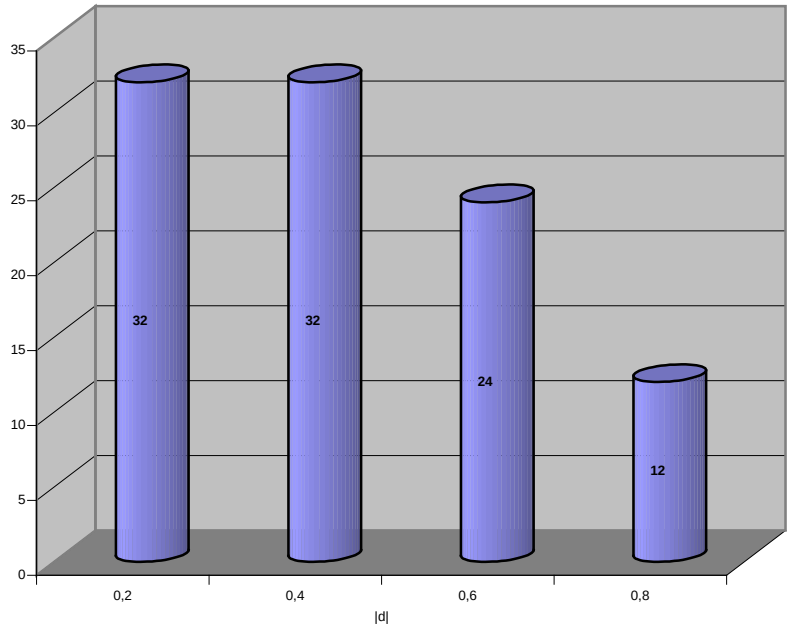
$$s = \sqrt{\frac{\sum_{i=1}^{n} [RON\,(GC)_i - RON(ASTM)_i]^2}{n-1}} \qquad [3]$$

The ratio between RON determined experimentally and the one determined based on results of regression analysis is shown in Figure 2. The standard ASTM method states that the reproducibility in 95% of the samples tested is up to 0.6, i.e. 0.7 octanes for RON values of 90 and 95 octanes respectively. The absolute aberration value of the calculated RON values is in 88% of the samples treated within 0.6 octanes, showing a very good match (Figure 3).

The repeatability of defining RON has been checked on a FCC gasoline sample (ASTM RON = 92.0) five times under the same experimental conditions. The average RON value of 92.10 octanes was obtained, and the standard deviation of

0.172. The regression equation was checked on a group of FCC gasolines and the average aberration of 0.25 octanes was obtained.

Figure 3: sample distribution per absolute aberration values



CONCLUSION

For the purpose of setting up the correlation of FCC gasoline composition with RON, the components separated in FCC gasoline were distributed into 46 groups encompassing 70-80 mass.% of the sample. The defined groups were assigned their accompanying hydrocarbon type determined according to the hydrocarbon or the complex which is the most represented in the group. Their sum provided 5 independent variables entering the regression analysis.

The linear regression analysis has provided the equation for calculating RON based on the chemical composition. The absolute aberration value for 88% of the samples treated is up to 0.6 octanes, while the calculated repeatability is 0.172.

The regression equation has been checked on a group of FCC gasolines and the average aberration of 0.25 octanes was obtained.

The method has been developed for laboratory monitoring of the process and does not require a big sample volume (0.2μl). It is also suitable for everyday characterization of the treatment process.

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