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KARAKTERIZACIJA TEKUĆIH PRODUKATA KREKIRANJA KROMATOGRAFSKIM METODAMA (HPLC, GC)

Sažetak

Proces fluid katalitičkog krekiranja (FCC) glavni je konverzijski proces u kojem se teške frakcije nafte konvertiraju u lakše frakcije. Tekući produkti katalitičkog krekiranja, FCC benzin i lako cikličko ulje koriste se za namješavanje motornog benzina ili dizelskog goriva. Strogom ekološkom i zakonskom regulativom zahtijeva se smanjenje količine sumpora te teško izgorivih aromata i olefina u motornim gorivima.

Kromatografskim tehnikama moguće je pratiti promjene sadržaja različitih grupa ugljikovodika pri katalitičkim reakcijama. U radu je prikazano određivanje grupnog sastava FCC benzina plinskom kromatografijom i sadržaja aromata prema broju aromatskih prstena u FCC benzinima, njihovim frakcijama i lakom cikličkom ulju tekućinskom kromatografijom. Uspoređeni su produkti krekiranja iz sirovina različitog porijekla (visoko sumporna i nisko sumporna nafta).

UVOD

Jedan od glavnih konverzijskih procesa pri preradi nafte je fluid katalitički krekning (FCC). Tim se procesom teške frakcije nafte koje sadrže i velike količine sumpornih i dušikovih spojeva konvertiraju u lakše frakcije te se tako povećava iskorištenje različitih naftnih produkata. Dio tekućih produkata katalitičkog krekiranja, FCC benzin (frakcije do 216 °C) i lako cikličko ulje (frakcije od 216 do 330 °C) koriste se za namješavanje motornog benzina i dizelskog goriva. FCC benzin namješava se u motorni benzin do 40% v/v, a značajno utječe na ukupnu količinu sumpora u motornom benzinu. Na vrijednost oktanskog broja motornog benzina utječe udio aromatskih ugljikovodika u FCC benzinima (tablica 1)^{1,2}.

Tablica 1: Količina aromatskih ugljikovodika i oktanski broj FCC benzina
 Table 1: Content of aromatic hydrocarbons and octane number of FCC gasoline

Sastav (% m/m) Composition (% m/m)	Uzorak benzina / gasoline sample		
	1	2	3
Količina aromata (% m/m) Aromatic content (% m/m)	34,4	26,0	25,4
Octane number	94,0	92,0	90,6

Zahtjevi kvalitete za ekološki prihvatljivim motornim gorivima ponukali su prerađivače na temeljitiju karakterizaciju krekiranih naftnih produkata s FCC-a i drugih konverzijskih procesa. Poznavanje kemijskog sastava produkata kreiranja doprinosi pojašnjenju mehanizama kemijskih reakcija koje se odvijaju za vrijeme procesa konverzije. Krekirani se produkti sastoje od parafinskih, olefinskih, aromatskih i polarnih ugljikovodika, što daje kompleksnu smjesu sa širokim rasponom kemijskih spojeva. Istraživanja i kvantitativna određivanja sastava ugljikovodika tih produkata u prisutnosti olefina je zahtjevno jer ne postoji jednostavna kemijska ili instrumentalna metoda koja može omogućiti kvantitativno određivanje svih grupa ugljikovodika u tako kompleksnim produktima.

Za određivanje grupnog sastava ugljikovodika u FCC produktima koriste se razne kromatografske tehnike. U nekim slučajevima te tehnike omogućuju odvajanje i određivanje pojedinih komponenata. No, kako primjenska svojstva fosilnih goriva i ulja ne ovise o pojedinim komponentama već o određenim grupama, popularno je kromatografsko određivanje grupnog sastava ugljikovodika prema polarnosti, aromatičnosti, broju C atoma i sl.

Zadatak rada je odrediti grupni i pojedinačni sastav uzoraka iz FCC procesa, kao i uzoraka frakcijske destilacije nakon tih procesa tehnikama tekućinske i plinske kromatografije. Kao sirovine u FCC procesima koriste se plinska ulja dobivena iz nisko i visoko sumpornih nafti.

EKSPERIMENTALNI DIO

Tekućinskom kromatografijom visoke djelotvornosti normalnih faza (HPLC-NP) određena je količina aromata u uzorcima FCC benzina i lakog cikličkog ulja. Određivanje je temeljeno na normi EN 12916³, iako je norma namijenjena samo srednjim (dizelskim) frakcijama⁴. Separacija se provodi na polarnoj silika ili modificiranoj polarnoj silika koloni uz nepolarnu pokretnu fazu. Kolona ne pokazuje afinitet za parafine (alifatske i cikličke), ali pokazuje naglašeni afinitet i selektivnost za aromatske ugljikovodike. Kao rezultat selektivnosti aromati su separirani od parafina i međusobno jasno odvojeni izraženim pikovima sukladno broju prstena, tj. kao mono-, di- i tri+ aromati. Tri+ aromati eluiraju kao zaseban oštar pik zahvaljujući uporabi povratnog ventila koji nakon eluiranja diaromata mijenja smjer protoka mobilne faze. Poliaromatski ugljikovodici (poliaromati, PAH) definirani su kao suma diaromata i tri+aromata, a ukupni aromati definirani su kao suma poliaromata i

monoaromata. Detekcija aromatskih grupa izvedena je RI i UV detektorima. RI detektor indeksa loma primijenjen je za uzorke s višim udjelom aromata, a UV ultra ljubičasti korišten za uzorke s nižim udjelom aromata.

PRIPREME UZORAKA I NP-HPLC ANALIZE

Uzorci se izvažu, otope u n-heptanu i nakon sušenja na Na_2SO_4 , bezvodni filtriraju preko membranskog filtra veličine pora 0.45 μm . 10 μL otopine uzorka injektira se u sustav koji se sastoji od pumpe, injektora, kolone i detektora te se komponente separiraju na μ -Bondapack NH_2 koloni (Waters) uz n-heptan kao mobilnu fazu. Kolona je termostatorana na 27 °C. Povratnim ventilom mijenja se smjer protoka mobilne faze nakon izlaženja di-aromata. Detektori su RI i UV ($\lambda = 254 \text{ nm}$). Cijeli sustav vođen je računalnim sustavom sa softverskom podrškom STAR 4.5 (Varian). Kako bi se odredilo vrijeme uključivanja povratnog ventila pri kalibraciji i analizama te rezolucija između cikloheksana i o-ksilena (minimalna 5.0), pripremljen je sistemski kalibracijski standard (SCS) (cikloheksan, o-ksilen, dibenzotiofen i 9-metilantracen).

Rezultati su kvantificirani kao % m/m metodom vanjskog standarda. Pripremljene su otopine kalibracijskih standarda i napravljene kalibracijske krivulje. Kao standardi korišteni su o-ksilen (mono-), 1-metilnaftalen (di-) i fenantren (tri+). Rezultati UV detektorom su određeni na osnovi apsorbancije pri 254 nm.

PLINSKO KROMATOGRAFSKE ANALIZE

Plinskom kromatografijom visokog razlučivanja na kapilarnoj kromatografskoj koloni SPB1 duljine 60 m, uzorci FCC benzina odijeljeni su na više od 300 pojedinačnih komponenata. Kromatografska kolona ima svojstvo odjeljivanja prema rastućem vrelištu.

Iz jedne plinskokromatografske analize moguće je istovremeno dobiti podatke o udjelu n-parafina, izoparafina, cikloparafina, olefina i aromata, te ukoliko je potrebno i podatke o koncentraciji pojedinih komponenata sadržanih u jednoj od navedenih grupa ugljikovodika. Određivanje grupnog sastava FCC benzina provodi se na osnovi pojedinačnog sastava grupiranjem spojeva prema tipu ugljikovodika.

Struktura i tip ugljikovodika pojedinačno odijeljenih komponenata provedena je na osnovi podataka o vremenu zadržavanja čistog spoja (Kovatsevi indeksi), podataka iz spektara masa dobivenih vezanim sustavom plinska kromatografija-spektrometrija masa, podataka dobivenih tekućinskom kromatografijom na stupcu (FIA), te podataka dobivenih na osnovi bromiranja nezasićene frakcije benzina.

Uzorci se analiziraju direktnim injektiranjem bez prethodne obrade, a uvjeti analize podešeni su tako da pružaju optimalan omjer između kvalitete odjeljivanja pikova, trajanja analize i primijenjenih uvjeta snimanja uzoraka.

UZORCI**A** - FCC sirovina i njezini produkti iz visoko sumporne nafte**B** - FCC sirovina i njezini produkti iz nisko sumporne nafte

Tablica 2: Radni uvjeti

Table 2: Operating conditions

NP-HPLC UVJETI/CONDITIONS		GC UVJETI/CONDITIONS	
KOLONA COLUMN	μ -Bondapak NH ₂ (Waters), dimenzije kolone 300 mmx3,9 mm, 10 μ m	KOLONA COLUMN	SPB-1, SUPELCO, 60 m promjer 0,32 mm debljina filma stacionarne faze – 0,25 μ m temperatura 20 °C, 2 °C/min - 220 °C (15 min)
MOBILNA FAZA MOBILE PHASE	n-heptan, HPLC čistoće, (priprema mobilne faze- propuhivanje helijem) n-heptane, HPLC purity, (preparation of mobile phase- blowing by helium)	PLIN NOSILAC CARRIER GAS	helij, protok na spliteru 17.5 ml/min helium, flow on splitter 17.5 ml/min
PROTOK MOBILNE FAZE FLOW OF MOBILE PHASE	0.8 ml/min	INJEKTOR	split/splitless, temperatura 250 °C
TEMPERATURA		DETEKTOR	plameno ionizacijski/gasionization (FID) temperatura 280 °C
KOLONA/COLUMN	27 °C		
INJEKTOR	27 °C		
DETEKTOR	indoors		
REZOLUCIJA (cikloheksan/o-ksilen)	5,4		
VRIJEME UKLJUČIVANJA POVRATNOG VENTILA TIME OF SWITCH-ON RETURN VALVE	9,74 min		
VRIJEME JEDNE ANALIZE TIME FOR ONE ANALYSIS	22,5 min		

REZULTATI I RASPRAVA

Kromatografski su analizirani tekući produkti kreiranja FCC sirovina, FCC benzin i lako cikličko ulje (LCU). Iz rezultata u tablici 3 vidljivo je da je FCC benzin bogatiji monoaromatskom frakcijom dok je LCU znatno bogatije poliaromatskim ugljikovodicima.

Uspoređivanjem rezultata analiza FCC benzina i LCU iz FCC sirovina s različitim sadržajem sumpora (tablice 3 i 4), ustanovljeno je da je sadržaj poliaromata i ukupnih aromata veći kod FCC produkata dobivenih iz visoko sumporne sirovine dok je udio monoaromata niži.

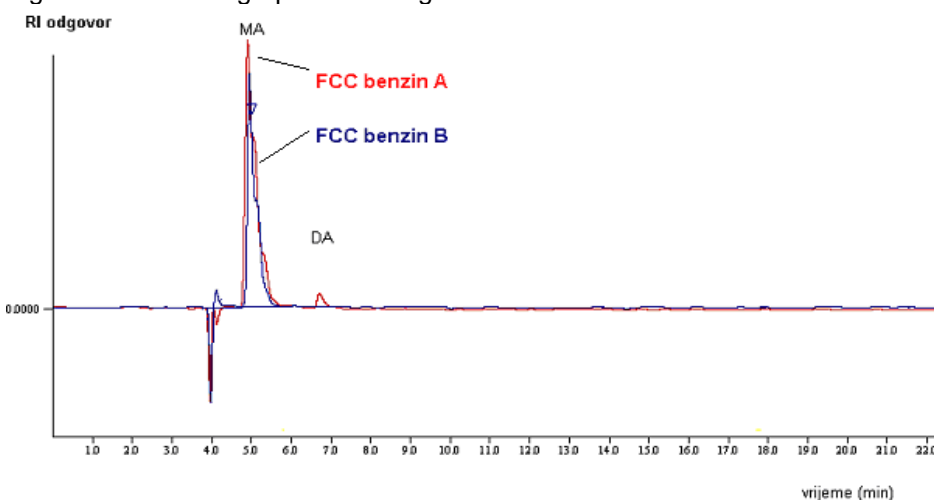
Tablica 3: Grupni sastav aromatskih ugljikovodika (% m/m) u katalitičkim produktima sirovine A (HPLC metoda RI detekcija)

Table 3: Group composition of aromatic hydrocarbons (% m/m) in catalytic products of feed A (HPLC method with RI detection)

Sastav % m/m Composition % m/m	mono- aromati	diaromati	tri+aromati	poliaromati	ukupni aromati total aromatics
FCC benzin A FCC gasoline A	28,12	0,72	0,07	0,79	28,91
LCU A / LCO A	17,10	54,48	2,07	56,55	73,65

Slika 1: Kromatogrami FCC benzina dobiveni HPLC-om, uz RI detektor

Figure 1: Chromatographs of FCC gasoline obtained on HPLC with RI detector



Tablica 4: Grupni sastav aromatskih ugljikovodika (% m/m) u katalitičkim produktima sirovine B (HPLC metoda RI detekcija)

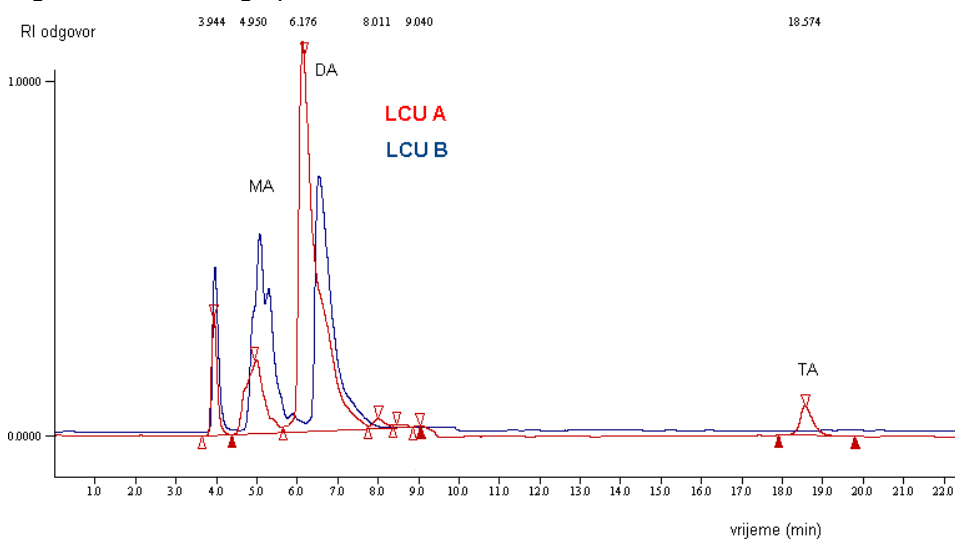
Table 4: Group composition of aromatic hydrocarbons (% m/m) in catalytic products of feed B (HPLC method with RI detection)

Sastav % m/m Composition % m/m	monoaromati	diaromati	tri+aromati	poliaromati	ukupni aromati total aromatics
FCC benzin B FCC gasoline B	20,96	0,18	0,12	0,30	21,26
LCU B / LCO B	39,26	31,14	0,07	31,21	70,47

Nakon frakcijske destilacije FCC benzina dobivenih iz sirovine A, frakcije su odvojeno analizirane na HPLC UV detektorom ($\lambda = 254$ nm). Analizom frakcija destilacije FCC benzina utvrđeno je da sadržaj aromatskih ugljikovodika raste s porastom temperature destilacije frakcije (tablica 5).

Slika 2: Kromatogrami LCU dobiveni HPLC-om, uz RI detektor

Figure 2: Chromatographs of LCU obtained on HPLC, with RI detector

Tablica 5: Grupni sastav aromatskih ugljikovodika (% m/m) frakcija destilacije FCC benzina (HPLC metoda UV/DAD, $\lambda = 254$ nm)Table 5: Group composition of aromatic hydrocarbons (% m/m) FCC gasoline distillation fractions (HPLC method with UV/DAD, $\lambda = 254$ nm)

Sastav % m/m Composition % m/m	mono aromati	diaromati	tri+aromati	poliaromati	ukupni aromati total aromatics
FCC benzin A/gasoline frakcija do 70 °C	3,252	0,223	0,015	0,238	3,490
FCC benzin A/gasoline frakcija od 70 do 110 °C	14,438	-	0,003	0,003	14,441
FCC benzin A/gasoline frakcija od 110 do 180 °C	60,130	0,569	0,008	0,577	60,707
FCC benzin B/gasoline frakcija do 70 °C	1,069	0,076	0,015	0,091	1,160
FCC benzin B/gasoline frakcija od 70 do 110 °C	13,236	0,031	-	0,031	13,267
FCC benzin B/gasoline frakcija od 110 do 163 °C	35,068	0,092	0,006	0,098	35,166

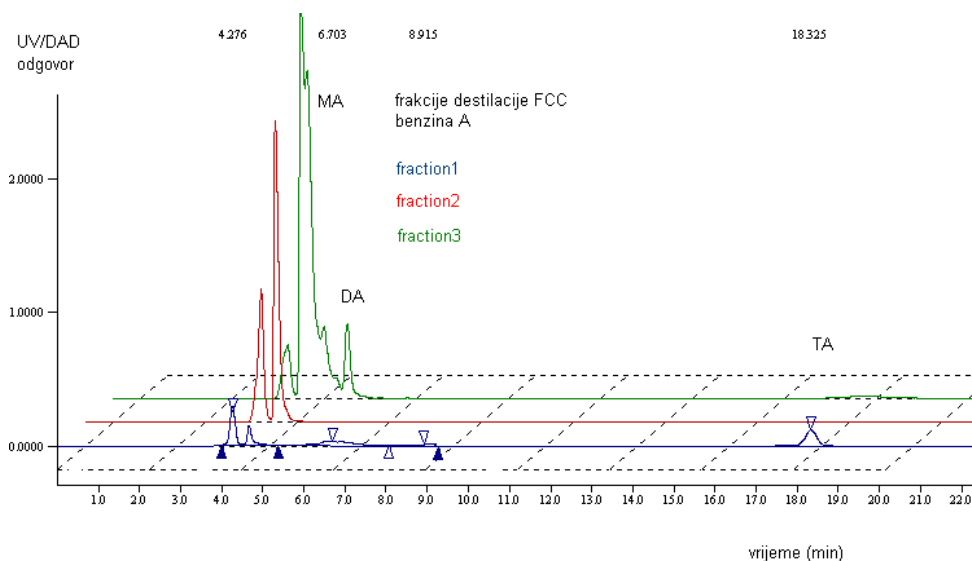
Sa stajališta GC analize FCC benzin je vrlo zahtjevna vrsta uzorka zbog svog kompleksnog sastava i opterećenosti nezasićenim ugljikovodicima posebice u lakšem dijelu frakcije. U ovom radu prikazan je način određivanja grupnog sastava FCC benzina na osnovi pojedinačnog sastava dobivenog plinskromatografskom analizom.

U tablicama 6 i 7 navedene su vrijednosti koncentracija grupa spojeva dobivenih plinskromatografskom analizom. Rezultati prikazani u tablici 7 pokazuju trend kretanja koncentracija pojedinih grupa ugljikovodika u određenom temperaturnom rezu, što je u korelaciji sa svojstvom primijenjene kolone koja komponente sadržane u uzorku odjeljuje prema rastućem vrelištu.

Vidljivo je da udio ukupnih parafina pada s povećanjem raspona vrelišta, a udjel ukupnih aromata u istim uvjetima frakcioniranja raste (tablica 5).

Slika 3: Kromatogrami frakcija destilacije FCC benzina A, HPLC uz UV/DAD ($\lambda = 254$ nm) detektoru

Figure 3: Chromatographs of FCC gasoline A distillation fractions, HPLC with UV/DAD ($\lambda = 254$ nm) detector



Tablica 6: Grupni sastav FCC benzina dobivenim iz različitih sumpornih sirovina tehnikom plinske kromatografije

Table 6: Group composition of FCC gasoline obtained from various sulphur feeds by gas chromatography

Sastav % m/m Composition % m/m	n-parafini	izoparafini	cikloparafini	n+izoparafini	olefini
FCC benzin A / gasoline	5,47	28,74	6,62	34,21	24,01
FCC benzin B / gasoline	6,42	35,92	7,52	42,34	22,18

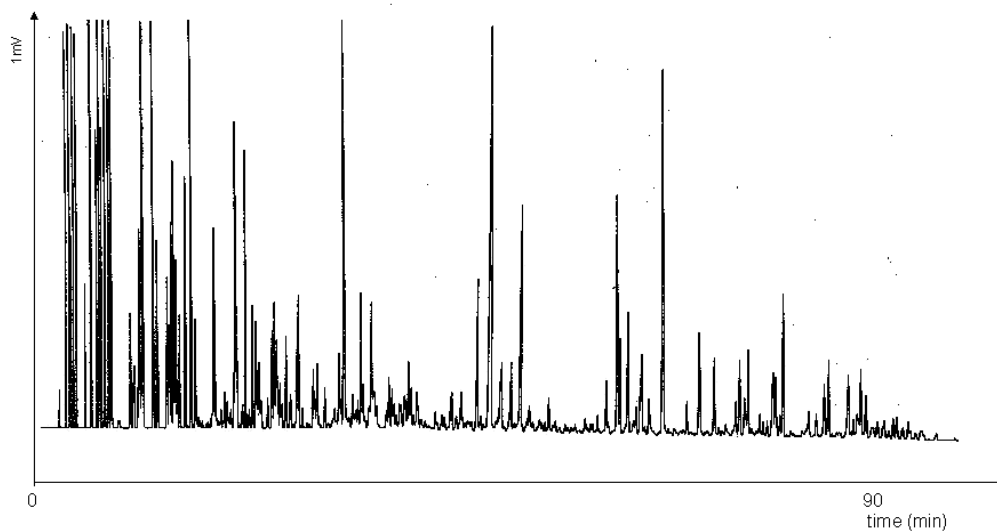
Tablica 7: Grupni sastav u destilacijskim frakcijama FCC benzina A plinskom kromatografijom

Table 7: Group composition in distillation fractions of FCC gasoline A by gas chromatography

Sastav % m/m Composition % m/m	n-parafini	izoparafini	cikloparafini	n+izoparafini	olefini
FCC benzin A/ gasoline frakcije od 0 to 150 °C	5,09	34,65	10,22	39,74	26,86
FCC benzin A/ gasoline frakcije od 0 do 160 °C	5,11	34,20	9,47	39,30	26,77
FCC benzin A/ gasoline frakcije od 0 do 172 °C	6,08	32,44	7,54	38,51	24,03
FCC benzin A/ gasoline frakcije od 0 do 180 °C	4,95	30,45	7,78	35,40	22,55
FCC benzin A/ gasoline frakcije od 0 do 190 °C	5,13	30,95	7,18	36,08	24,05

Slika 4: Tipičan kromatogram FCC benzina dobiven tehnikom plinske kromatografije

Figure 4: A typical chromatograph of FCC gasoline analyzed by gas chromatography



ZAKLJUČAK

Određen je pojedinačni i grupni sastav ugljikovodika tekućih FCC produkata koji se namješavaju u motorna goriva. Uspoređeni su FCC produkti dobiveni iz različitih sumpornih naftnih sirovina.

NP-HPLC metodom uz primjenu RI i UV/DAD detektora određen je sadržaj aromatskih ugljikovodika prema broju prstena u strukturi. Kombinacijom RI i UV/DAD detektora određeni su aromatski ugljikovodici u širokom koncentracijskom području, što uporabom jednog detektora nije moguće. Rezultati pokazuju da je sadržaj poliaromatskih ugljikovodika veći kod FCC produkata dobivenih iz visoko sumporne sirovine. Analiza frakcija FCC benzina pokazala je da sadržaj aromata raste s porastom temperature destilacije.

U radu je prikazan način određivanja grupnog sastava FCC benzina na osnovi pojedinačnog sastava dobivenog plinskrokromatografskom analizom. Na osnovi prikazanih podataka o grupnom sastavu uzoraka dobivenih kreiranjem visoko i nisko sumporne nafte može se pratiti kretanje koncentracija pojedinih grupa spojeva te na taj način dobiti vrijedni podaci pri optimiranju procesa kreiranja.

Kombiniranjem prikazanih rezultata plinske i tekućinske kromatografije postignut je potpuniji uvid u kompleksan sastav FCC produkata i mogućnost njihove primjene kao komponenata pri namješavanju motornih goriva.

CHARACTERIZATION OF LIQUID CRACKING PRODUCTS USING CHROMATOGRAPHIC METHODS (HPLC, GC)

Abstract

The process of fluid catalytic cracking (FCC) is the main conversion process in which heavy oil fractions convert into lighter fractions. Liquid catalytic cracking products, FCC gasoline and light cyclic oil, are used for blending motor gasoline or diesel fuel. Stringent environmental and legal regulations require reduction of the content of sulphur and hardly combustible aromatics and olefins in motor fuels. Chromatographic techniques make it possible to monitor changes in the content of various hydrocarbons groups at catalytic reactions. The paper presents the determination of group composition of FCC gasoline through gas chromatography, and that of aromatic content according to the number of aromatic rings in FCC gasolines, their fractions and light cyclic oil, using liquid chromatography. Compared were cracking products obtained from feeds of various origins (high sulphur and low sulphur oil).

INTRODUCTION

One among the main conversion processes at oil processing is fluid catalytic cracking (FCC). The process converts heavy oil fractions containing large volumes of sulphur and nitrogen compounds into lighter fractions thus increasing the use of different oil products. A part of liquid catalytic cracking products, FCC gasoline (fractions up to 216°C) and light cyclic oil (fractions from 216 to 330°C) are used for the blending of motor gasoline and diesel fuel. FCC gasoline is blended into motor gasoline up to 40% (v/v), while it has a considerable impact on total sulphur content in motor gasoline. The motor gasoline octane number is also influenced by the share of aromatic hydrocarbons in FCC gasoline (Table 1)^{1,2}.

Quality requirements for environmentally tolerable motor fuels have prompted the refiners to undertake a more thorough characterization of cracked oil products from FCC and other conversion processes. The knowledge of the chemical composition of cracking products contributes to the clearance of mechanisms of chemical reactions taking place during the conversion process. The cracked products consist of saturated, olefinic, aromatic and polar hydrocarbons, providing a complex blend with a wide range of chemical compounds. Investigation and quantitative determination of hydrocarbon composition of these products in the presence of olefins is demanding, because there is no single chemical or instrumental method which could enable quantitative determination of all hydrocarbon groups in such complex products.

For the determination of group composition of hydrocarbons in FCC products, different chromatographic techniques are being used. In some cases, these techniques enable separation and identification of individual components. However, since the applicative properties of most fossil fuels and oils do not depend on individual components but on specific groups, popular is the chromatographic determination of group hydrocarbon composition according to polarity, aromaticity, number of C atoms, and the like.

The aim of the paper is to determine group and individual composition of FCC process samples, as well as samples of fraction distillation after these processes using liquid and gas chromatography. As feeds in FCC processes, oils are used, obtained from low and high sulphur feeds.

THE EXPERIMENTAL PART

High efficiency liquid chromatography of normal phases (NP-HPLC) was used to determine the volume of aromatics in FCC gasoline and light cyclic oil. Determination was based on EN 12916 standard³, although the standard is intended solely for medium (diesel) fractions⁴. Separation is performed on a polar silica or modified polar silica column, with a non-polar movable phase. The column does not show affinity for paraffins (aliphatic and cyclic), but it does show a pronounced affinity and selectivity for aromatic hydrocarbons. As a result of selectivity, aromatics

are separated from paraffins and mutually clearly separated by pronounced peaks in keeping with the number of rings i.e. as mono-, di- and tri+ aromatics. Tri+ aromatics eluate as a separate sharp peak owing to the use of return valve which after the eluation of di-aromatics changes the direction of mobile phase flow. Poly-aromatic hydrocarbons (poly-aromatics, PAH) are defined as the sum of di-aromatics and tri+aromatics, while total aromatics are defined as the sum of poly-aromatics and mono-aromatics. Detection of aromatic groups was performed using RI and UV detectors. RI refractive index detector was applied for samples with higher aromatic content, while UV ultraviolet detector was used for samples with lower aromatic content.

PREPARATION OF SAMPLES AND NP-HPLC ANALYSIS

The samples are weighted, dissolved in n-heptane and, after drying on Na₂SO₄, anhydrous filtered through a membrane filter with pore size of 0.45µm. 10µL of sample solution is injected into the system consisting of pump, injector, column and detector, and the components are separated on µ-Bondapack NH₂ column (Waters), with n-heptane as mobile phase. The column was thermostated at 27°C. Return valve changes the direction of mobile phase flow after isolation of di-aromatics. The components were detected using RI and UV detectors (λ=254nm). The entire system was conducted by a computer system with software support STAR 4.5 (Varian).

In order to determine the time of return valve switching on at calibration, and analyses and resolution between cyclohexane and o-xylene (minimum 5.0), a system calibration standard (SCS) (cyclohexane, o-xylene, dibenzotiofene and 9-methylantracene) was prepared.

The results were quantified as %m/m, using the method of outer standard. Prepared were solutions of calibration standards and calibration curves made. Used as standard were o-xylene (mono-), 1-methylnaphtalene (di-) and fenentrene (tri+). The results of UV detectors were determined based on absorbance at 254 nm.

GAS CHROMATOGRAPHY ANALYSES

High resolution gas chromatography on a capillary chromatographic column SPB1 60 m long separates FCC gasoline samples into over 300 individual components. The chromatographic column has the property of separation according to the increasing flash point. One gas chromatographic analysis makes it possible to simultaneously obtain data on the content of n-paraffins, iso-paraffins, cyclo-paraffins, olefins and aromatics, and – if necessary - also data on the concentration of individual components contained in one of the said hydrocarbon groups. Determination of FCC gasoline group composition is performed based on individual composition by grouping compounds according to hydrocarbon type.

The structure and type of hydrocarbons of individually separated components was performed based on data of the time for maintaining clear compound (Kovats'

indices), data from mass spectra obtained by linked system gas chromatography-mass spectrometry, data obtained by column liquid chromatography (FIA), and data obtained that are based on bromiding unsaturated gasoline fraction.

Samples are analyzed through direct injection without preliminary treatment, while the analysis conditions are set so as to offer an optimal ratio between peaks separation quality, analysis duration and applied conditions of sample registering.

SAMPLES

A – FCC feed and its products from high sulphur feed

B – FCC feed and its products from low sulphur feed

Conditions of gas chromatographic analysis are set so as to offer an optimal ratio between the quality of separating peaks, duration of analysis and applied analysis conditions.

RESULTS AND DISCUSSION

Chromatographic analysis was performed on liquid cracking products of FCC feeds, FCC gasoline and light cyclic oil (LCO). The results in Table 3 show that FCC gasoline is richer with mono-aromatic fraction while LCO is much richer in poly-aromatic hydrocarbons.

By comparing results of analyses of FCC gasoline and LCO from FCC feeds with different sulphur content (Tables 3 and 4), it has been established that the content of poly-aromatics and total aromatics is higher for FCC products obtained from the feed richer in sulphur, while the share of mono-aromatics is lower.

Following fractional distillation of FCC gasoline obtained from feed A, fractions were analyzed separately using HPLC UV detector ($\lambda=254\text{nm}$). Analysis of fractional distillation of FCC gasoline has shown that the content of aromatic hydrocarbons increases with the increase of fractional distillation temperature (Table 5).

From the viewpoint of GC analysis FCC gasoline is a highly demanding kind of sample due to its complex composition and being burdened with unsaturated hydrocarbons, especially in the lighter part of the fraction. Shown in the present paper is the manner of determining group composition of FCC gasoline based on individual composition obtained by gas chromatographic analysis.

Tables 6 and 7 list the values of concentrations of groups of compounds obtained by gas chromatographic analysis. The results shown in Table 7 show the trend of concentration development of individual hydrocarbon groups within a given temperature section which may be correlated with the property of applied column separating components contained in injected sample according to the increasing flash point.

It may be observed that the share of total paraffins decreases with increased flash point range, while the content of total aromatics under the same fractionation conditions increases (Table 5).

CONCLUSION

Determined was both group and individual composition of hydrocarbons of liquid FCC products blended into motor fuels. Compared were FCC products obtained from various sulphur oil feeds.

NP-HPLC method, with the application of RI and UV/DAD detectors, has determined the composition of aromatic hydrocarbons according to the number of rings in the structure. Through a combination of RI and UV/DAD detectors aromatic hydrocarbons in a wide concentration area were determined, which is not possible with the use of a single detector. The results show that the composition of poly-aromatic hydrocarbons is higher for FCC products obtained from the high sulphur feed. The analysis of fractions of FCC gasoline has shown that the aromatic content increases with distillation temperature increase.

The paper presents the determination of FCC gasoline group composition based on individual composition obtained by gas chromatographic analysis. Based on the data shown on the group composition of samples obtained by cracking of high and low sulphur content in oil it is possible to monitor the development of concentrations of individual compound groups, and thus obtain valuable data in optimizing the cracking process.

By combining the shown results of gas and fluid chromatography, we have obtained a more complete insight into the complex composition of FCC products, and hence also the possibility of their application as components in the blending of motor fuels.

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