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SEPARACIJA I KARAKTERIZACIJA AROMATSKIH FRAKCIJA IZ FCC SIROVINE I PRODUKATA

Sažetak

FCC proces ili fluid katalitički kreking jedan je od glavnih rafinerijskih procesa, u kojem se konvertiraju teška plinska ulja u mnogo vrjednije produkte poput FCC benzina. Da bi se udovoljilo strogim ekološkim zahtjevima koje propisuju međunarodne specifikacije, potrebno je u motornim gorivima, čija je komponenta i FCC benzin, smanjiti količinu sumpora, aromata i olefina.

Porijeklo i tip sirovine koja se koristi pri katalitičkom krekiranju utječu na raspodjelu i količinu aromatskih ugljikovodika u nastalim produktima. Kromatografskim tehnikama kao što su tekućinska kromatografija i vezana tehnika GC/MS moguće je pratiti kemizam nastajanja i transformacije različitih aromatskih spojeva iz FCC sirovine u nastale produkte krekiranja kao što su FCC benzin i lako cikličko ulje (LCU).

Iz dvije FCC sirovine dobivene iz nafti različitog porijekla razdvojeni su asfalteni od maltena. Iz frakcije maltena odvojene su frakcije zasićenih, aromatskih i polarnih ugljikovodika na polupreparativnoj koloni metodom tekućinske kromatografije. Frakcija aromatskih ugljikovodika odvojena je na mono, di, tri+ aromate koji su kvantitativno određeni analitičkom tekućinskom kromatografijom te analizirani vezanim sustavom GC/MS kako bi se i kvalitativno odredili. Produkti katalitičkog krekiranja dobiveni iz FCC sirovina FCC benzin i lako cikličko ulje također su analizirani navedenim tehnikama te su uspoređeni dobiveni rezultati.

Uvod

Fluid katalitički kreking (FCC) jedan je od najvažnijih kreking procesa za konverziju teških destilacijskih ostataka (t_v=250-600^{o}C; teško plinsko ulje, vakuum plinsko ulje i ostaci) u lakše frakcije nižeg vrelišta (benzin i lako cikličko ulje).

Poznavanje kemijskog sastava sirovine i krekiranih produkata igra značajnu ulogu u poznavanju kemije reakcija koje se odvijaju za vrijeme procesa krekinga pod različitim operacijskim uvjetima.

FCC produkti složene su ugljikovodične smjese koje sadržavaju zasićene ugljikovodike, aromate, polarne spojeve te olefine koji nastaju u kreking reakcijama. Sadržaj aromata i olefina zajedno sa zasićenim ugljikovodicima utječu na konačna svojstva goriva.

Dio tekućih produkata katalitičkog krekiranja, FCC benzin (frakcije do 216 ^{o}C) i lako cikličko ulje (frakcije od 216 do 330 ^{o}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[1] (tablica 1).

Tablica 1: Količina aromatskih ugljikovodika i oktanski broj FCC benzina

	Uzorak benzina		
Sastav (% m/m)	1	2	3
Količina aromata (%, m/m)	34,4	26,0	25,4
Oktanski broj	94,0	92,0	90,6

Zbog zahtjeva kvalitete za ekološki prihvatljivim motornim gorivima nužna je karakterizacija FCC sirovina i produkata.

Polupreparativnom NP HPLC sakupljane su veće količine frakcija za GC/MS analizu.

Analitička tekućinska kromatografija visoke djelotvornosti normalnih faza (NP HPLC) i kapilarna plinska kromatografija u off-line modu su komplementarne tehnike što ih čini prikladnima za određivanje grupnog sastava zasićenih ugljikovodika, mono-, di- i tri+ aromata te pojedinačnog sastava velikog broja ugljikovodičnih komponenti.

Vezani sustav plinske kromatografije i masene spektrometrije (GC/MS) daje nam daljnje informacije o pojedinačnom sastavu.

U radu su karakterizirane dvije različite sirovine dobivene iz Russian Export Blend (REB) smjese nafti i Syria light nafte prije krekiranja u industrijskom postrojenju te njihovi produkti- FCC benzin i lako cikličko ulje.

Eksperimentalni dio

FCC sirovine su prije kromatografske separacije podvrgnute deasfaltaciji kako bi se uklonili u n-heptanu netopljivi asfalteni, a maltenski dio separiran je i karakteriziran kromatografskim tehnikama.

Polupreparativna HPLC izvedena je modifikacijom EN 12916 na Agilent 1100 tekućinskom kromatografu uz povratni ventil. Vrijeme uključivanja povratnog ventila mijenjano je, kako bi se postigla što veća čistoća separiranih ugljikovodičnih frakcija.

Analitička NP HPLC izvedena je na amino modificiranoj silica gel koloni s n-heptanom kao mobilnom fazom uz detektor indeksa loma (RI) i povratni ventil na tekućinskom kromatografu tvrtke Varian, a sukladno EN 12916. Kolona ne pokazuje afinitet za zasićene ugljikovodike, 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.

GC/MS analiza izvedena je na temperaturno programiranoj kapilarnoj koloni duljine 60m i masenim spektrometrom s ion trap analizatorom uz jakost ionske struje 70 eV.

Tablica 2: Radni uvjeti

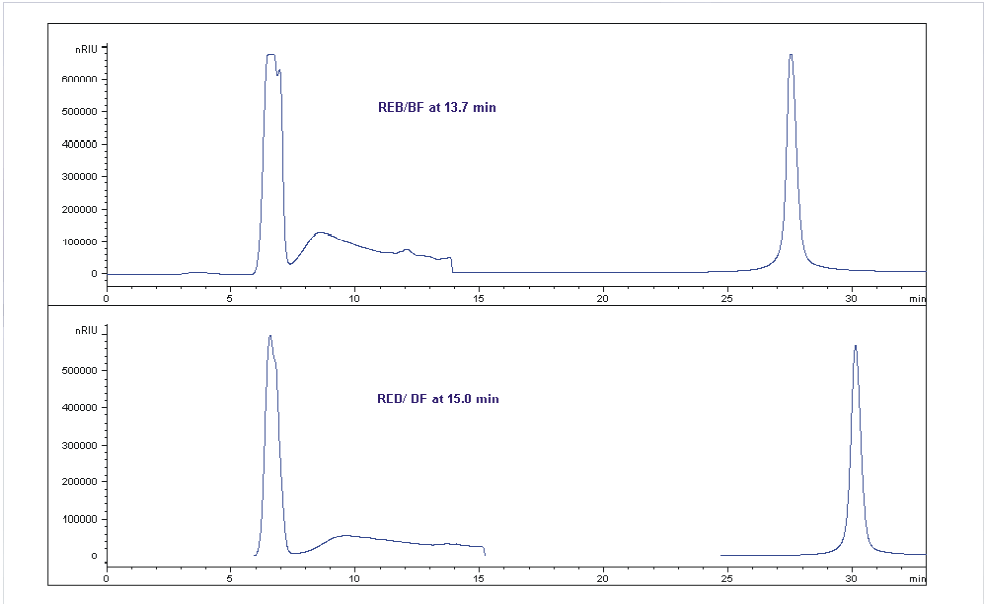
NP-HPLC UVJETI		GC/MS UVJETI	
KOLONA	µ-Bondapack NH_2 (Waters), dimenzije kolone 300 mmx3,9 mm, 10 µm	KOLONA	SPB-1, SUPELCO, 60 m promjer 0,32 mm debljina filma stacionarne faze – 1 µm temperatura
MOBILNA FAZA	n-heptan, HPLC čistoće, (priprema mobilne faze-propuhivanje helijem)	PLIN NOSILAC	helij
PROTOK MOBILNE FAZE	0.8 ml/min		narinuti tlak 20 psi
TEMPERATURA			
KOLONA	27 ^{O}C	KOLONA	10 ^{O}C, 2 ^{O}C/min - 220 ^{O}C (15 min)
INJEKTOR	27 ^{O}C	INJEKTOR	split/splitless, temperatura 250 ^{O}C
DETEKTOR	sobna temperatura	DETEKTOR	MS – ion trap, 70 eV, 1scan/s
REZOLUCIJA (cikloheksan/o-ksilen)	5,4		
VRIJEME UKLJUČIVANJA POVRATNOG VENTILA	9,74 min		
VRIJEME JEDNE ANALIZE	22,5 min		

Rezultati i rasprava

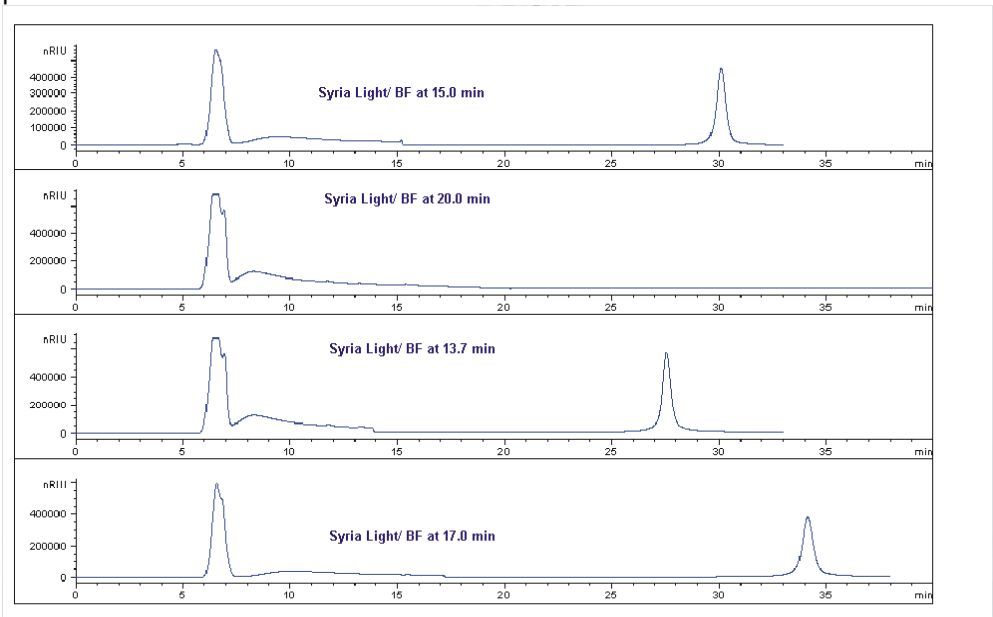
FCC sirovine i tekući produkti krekiranja FCC benzin i lako cikličko ulje (LCU) analizirani su kromatografskim tehnikama. Polupreparitivnom HPLC uz povratni ventil sakupljene su veće količine čistih frakcija ugljikovodičnih grupa koje su zatim analizirane analitičkom NP HPLC i GC/MS (slika 1 i 2).

Analitičkom NP HPLC dobiven je grupni sastav i sirovina i produkata (slika 3 i 4).

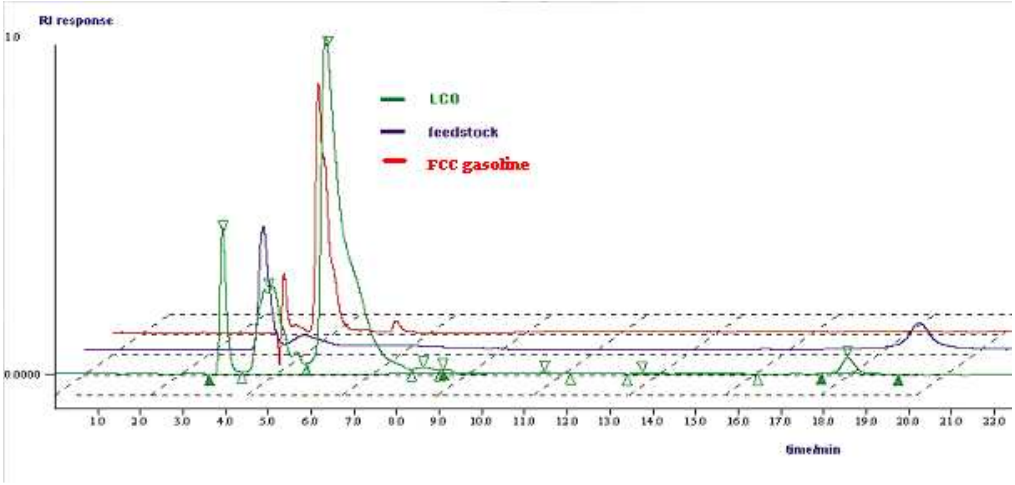
Slika 1: Polupreparativni kromatogram REB sirovine s različitim pozicijama povratnog ventila
Figure 1: Semi-preparational chromatograph of REB crude with various positions of return valve



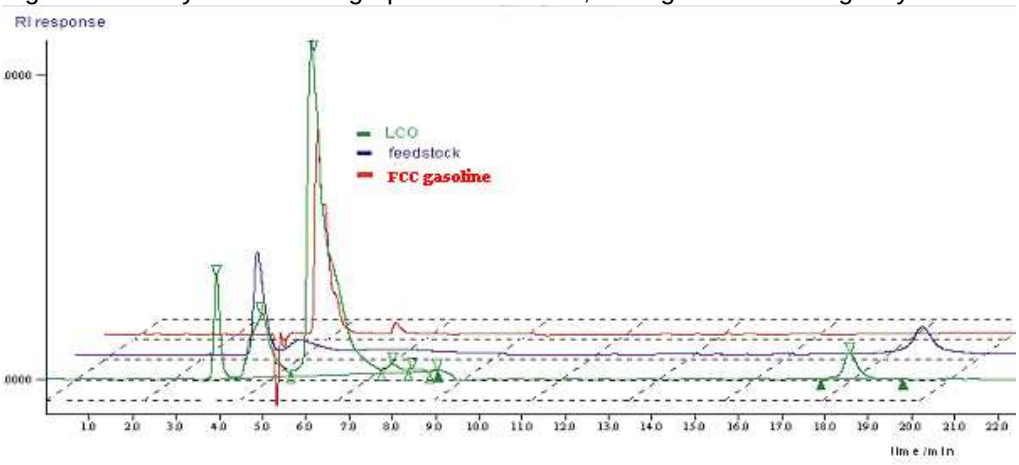
Slika 2: Polu-preparativni kromatogram Syria light sirovine s različitim pozicijama povratnog ventila
Figure 2. Semi-preparational chromatograph of Syria light crude with various positions of return valve



Slika 3: Analitički kromatogram Syria light, FCC benzina i lakog cikličkog ulja
Figure 3: Analitycal chromatograph of Syria light, FCC gasoline and light cyclic oil

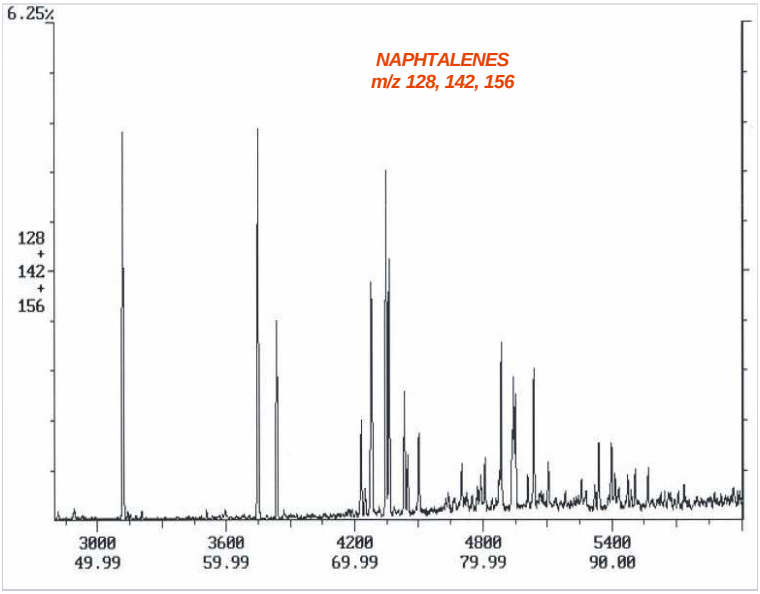


Slika 4: Analitički kromatogram REB sirovine, FCC benzina i lakog cikličkog ulja
Figure 4: Analitycal chromatograph of REB crude, FCC gasolin e and light cyclic oil

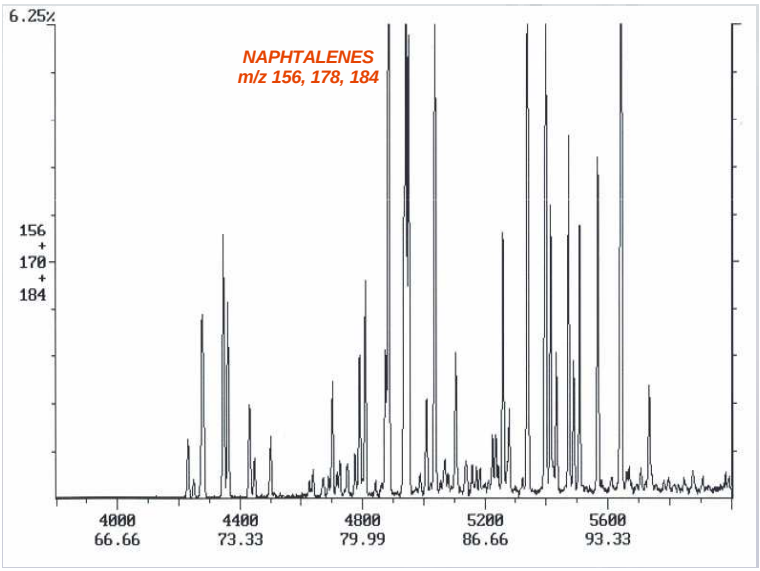


GC/MS analizom određene su homologne serije poliaromata poput naftalena, fenantrena i fluorena (slike 5,6,7,8,9), što je važno pri karakterizaciji FCC procesa.

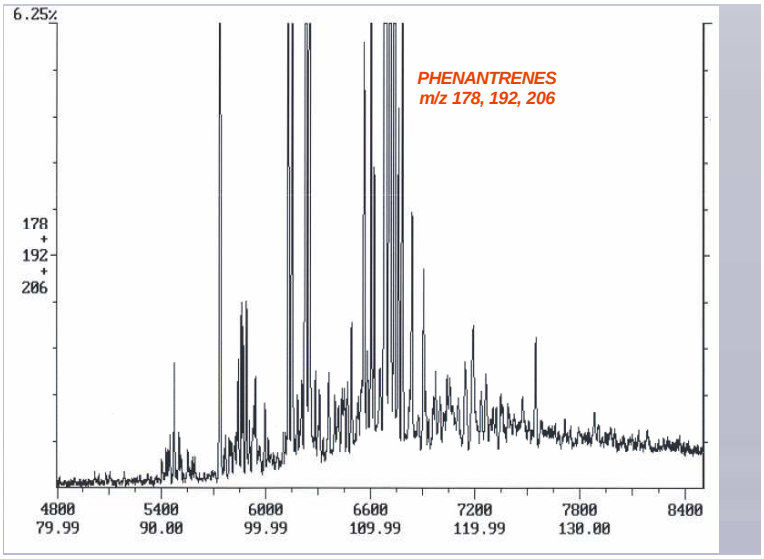
Slika 5: Kromatogram masa naftalena s m/z 128, 142, 156
Figure 5: Chromatograph of naphtalene mass, m/z 128, 142, 156



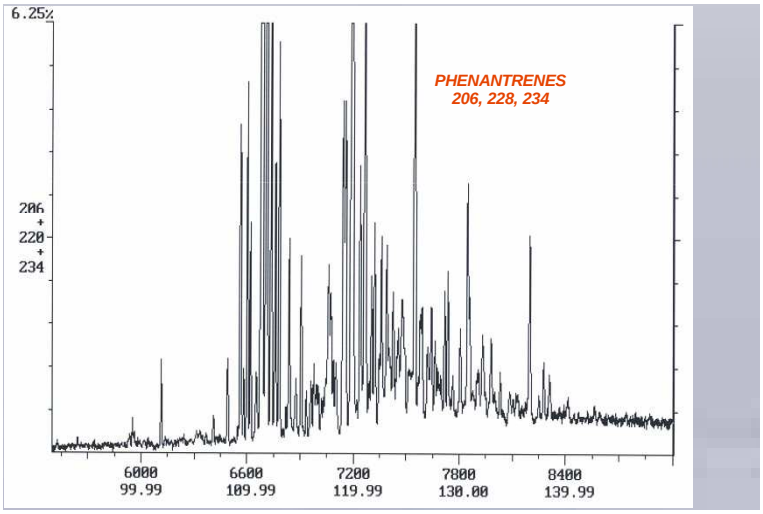
Slika 6: Kromatogram masa naftalena s m/z 156, 178, 184
Figure 6: Chromatograph of naphthalene mass, m/z 156, 178, 184



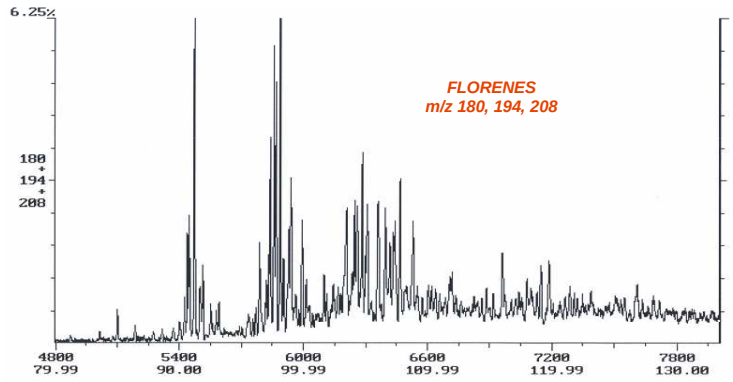
Slika 7: Kromatogram masa fenantrena s m/z 178, 192, 206
Figure 7: Chromatograph of phenantrene mass, m/z 178, 192, 206



Slika 8: Kromatogram masa fenantrena s m/z 206, 228, 234
Figure 8: Chromatograph of phenantrene mass, m/z 206, 228, 234



Slika 9: Kromatogram masa florena s m/z 180, 194, 208
Figure 9: Chromatograph of florene mass, m/z 180, 194, 208



NP HPLC rezultati ukazuju na različiti sastav grupa ugljikovodika i u FCC sirovinama i produktima. Aromati su određeni direktno, a zasićeni kao razlika do 100 %. (tab. 3)

Tablica 3: Sadržaj aromata u ispitivanim sirovinama i FCC produktima (NP HPLC/RID)

udio aromata, (% m/m)	FCC sirovina iz REB smjese nafte	FCC benzin iz REB smjese nafte	LCU iz REB smjese nafte	FCC sirovina iz Syria Light nafte	FCC benzin iz Syria Light nafte	LCU iz Syria Light nafte
monoaromati	17.7	28.1	17.1	14.8	23.9	23.6
diaromati	8.5	0.7	54.5	5.0	0.7	51.4
tri+aromati	10.4	0.1	2.1	9.7	-	1.0
poliaromati	18.8	0.8	56.6	14.7	0.7	52.4
ukupni aromati	36.6	28.9	73.7	29.5	24.6	76.0

Zasićeni ugljikovodici se za vrijeme katalitičkog procesa prevode u aromatske ugljikovodike i olefine, a kao rezultat toga je značajno povećanje aromatskih spojeva, a posebno poliaromata.

Uočeno je i određeno smanjenje ukupnog aromatskog sadržaja u lakšim FCC frakcijama (FCC benzin), premda je sadržaj monoaromata porastao u isto vrijeme.

Nastajanje monoaromata u FCC benzinu može se objasniti aromatizacijom cikličkih komponenata, oligomerizacijom i konverzijom zasićenih u naftenske komponente.

Prisutnost naftalena u tri+ aromatskoj frakciji može se objasniti nesavršenošću separacije na amino modificiranoj silka gel koloni te korigiranom položaju povratnog ventila.

Veliki sadržaj aromata u lakom cikličkom ulju pokazuju da se ta komponenta može koristiti pri namješavanju u dizelsko gorivo samo uz dodatno hidroobradu.

Zaključak

Kombiniranjem prikazanih rezultata plinske i tekućinske kromatografije postignut je potpuniji uvid u kompleksan sastav FCC sirovina i produkata. Poznavanje pojedinačnog i grupnog sastava aromatskih ugljikovodika u FCC sirovinama i frakcijama važno je za formuliranje parametara samog FCC procesa te predviđanje kvalitete i ekološke prihvatljivosti krajnjih komercijalnih produkata.

Praćenjem aromatskih grupa u lakšim FCC produktima ustanovljeno je smanjenje sadržaja ukupnih aromata uz istodobno povećanje sadržaja mono-aromata u odnosu na početnu sirovinu, dok je sadržaj aromata u cikličkom ulju istodobno povećan. Za namješavanje cikličkih ulja u dizelska goriva, sukladno aktualnim zahtjevima kvalitete, potrebna je dodatna obrada.

SEPARATION AND CHARACTERIZATION OF AROMATIC FRACTIONS FROM FCC FEED AND PRODUCTS

Abstract

FCC process is one among major refinery processes, converting heavy gas oils into much more valuable products, such as FCC gasoline. In order to meet stringent environmental requirements prescribed by international specifications, it is necessary to reduce motor fuel – its component being also FCC gasoline - sulphur, aromatics and olefins content.

The origin and type of feed used for catalytic cracking impacts the distribution and volume of aromatic hydrocarbons in generated products.

Chromatographic techniques, such as liquid chromatography and its associated technique of GC/MS, makes it possible to follow the chemistry of generation and transformation of different aromatic compounds out of FCC feed into generated cracking products, such as FCC gasoline and light cyclic oil (LCU).

Out of two FCC feeds obtained from different origin crudes, separated were asphaltenes from maltenes. From the fraction of maltenes separated were fractions of saturated, aromatic and polar hydrocarbons on a semi-preparative column using the method of liquid chromatography. Fraction of aromatic hydrocarbons was separated into mono, di, tri+ aromatics, whose volume was determined by analytical liquid chromatography, and analyzed by its associated system GC/MS, in order to determine their properties as well. Products of catalytic cracking obtained from FCC feeds: FCC gasoline and light cyclic oil, were also analyzed by the said techniques, and the obtained results were compared.

Introduction

Fluid catalytic cracking (FCC) is one among the most significant cracking processes for the conversion of heavy distillation residues (t_v=250-600^{o}C; heavy gas oil, vacuum gas oil and residues) into lighter fractions with lower boiling point (gasoline and light cyclic oil).

Knowledge of the chemical composition of the feed and of the cracking products plays a significant role in knowing the chemistry of reactions taking place during the process of cracking, under different operating conditions.

FCC products are complex hydrocarbon compounds containing saturated hydrocarbons, aromatics, polar compositions and olefins, generated through cracking reactions. The content of aromatics and olefins, together with saturated hydrocarbons, impacts the final fuel properties.

A part of the liquid products of catalytic cracking, FCC gasoline (fractions up to 216 ^{o}C) and light cyclic oil (fractions from 216 to 330 ^{o}C) are used for the blending of petrol or motor gasoline and diesel fuel. FCC gasoline is blended into petrol up to 40% v/v, while it has a considerable impact on total sulphur motor gasoline content. The octane number value of petrol is under the impact of the share of aromatic hydrocarbons in FCC gasoline[1] (Table 1).

Table 1: Volume of aromatic hydrocarbons and octane number of FCC gasoline

	Gasoline sample		
Composition (% m/m)	1	2	3
Aromatic content (%, m/m)	34,4	26,0	25,4
Octane number	94,0	92,0	90,6

Due to quality requirements for environmentally tolerable motor fuels, it is necessary to characterize FCC feeds and products.

Through semi-preparative NP HPLC, gathered were larger amounts of fractions for GC/MS analysis.

Analytical normal phase high performance liquid chromatography (NP HPLC) and capillary gas chromatogrphy in off-line mode are complementary techniques, which makes them suitable for the deternination of group composition of saturated hydrocarbons; mono-, di- and tri+ aromatics, as well as the individual composition of a large number of hydrocarbon components.

The connected system of gas chromatography and mass spectrometry (GC/MS) provides us with further information on individual composition.

The paper characterizes two different feeds obtained from the Russian Export Blend (REB) crude mix and Syria light crude, before cracking in the industral plant, and their products - FCC gasoline and light cyclic oil.

Experimental

FCC feeds were subjected to deasphaltation before the chromatographic separation, in order to remove n-heptane-insoluble asphaltenes, while the maltene part was separated and characterized through chromatographic techniques.

Semi-preparative HPLC was performed through a modification of EN 12916 to Agilent 1100 liquid chromatograph with return valve. The return valve switch timing has been modified, in order to obtain purity of separated hydrocarbon fractions as high as possible.

Analytical NP HPLC was performed on amino modified silica gel column with n-heptane as mobile phase, with refraction index detector (RI) and return valve on

liquid chromatograph made by "Varian", consistent with EN 12916. The column shows no affinity for saturated hydrocarbons, but it shows a considerable affinity and selectivity for aromatic hydrocarbons. As a result of selectivity, aromatics were separated from paraffins and mutually clearly separated through highlighted peaks depending on the ring number, i.e. as mono-, di- and tri+ aromatics.

GC/MS analysis was made on the temperature-programmed capillary column 60m long and mass spectrometer with ion trap analyzer, the ion current power being 70 eV.

Table 2: Operating conditions

NP-HPLC CONDITIONS		GC/MS CONDITIONS	
COLUMN	µ-Bondapack NH_2 (Waters), dimensions of column 300 mmx3,9 mm, 10 µm	COLUMN	SPB-1, SUPELCO, 60 m diameter 0.32 mm film thickness of stationary phase – 1 µm temperature
MOBILE PHASE	n-heptane, HPLC purity, (preparation of mobile phase- helium-blowing/?/)	CARRIER GAS	helium
MOBILE PHASE FLOW	0.8 ml/min		imposed pressure 20 psi
TEMPERATURE			
COLUMN	27 ^{O}C	COLUMN	10 ^{O}C, 2 ^{O}C/min - 220 ^{O}C (15 min)
INJECTOR	27 ^{O}C	INJECTOR	split/splitless, temperature 250 ^{O}C
DETECTOR	room temperature	DETECTOR	MS – ion trap, 70 eV, 1 scan/s
RESOLUTION (cyclohexan/o-xylene)	5,4		
TIME OF RETURN VALVE SWITCH ON	9,74 min		
TIME NEEDED FOR ANALYSIS	22,5 min		

Resuls and discussion

FCC feeds and liquid cracking products: FCC gasoline and light cyclic oil (LCU), were analyzed using chromatographic techniques. Using semi-preparitive HPLC with return valve, larger volumes of pure fractions of hydrocarbon groups were collected and subsequently analyzed using analytical NP HPLC i GC/MS (Figures 1 and 2).

Analytical NP HPLC provided the group composition of feeds and products (Figures 3 and 4).

GC/MS analysis determined homologous series of polyaromatics, such as naphthalene, phenantrene and fluorene (Figures 5, 6, 7, 8, 9), which may be of major importance in characterizing FCC processes.

P HPLC results point to a different composition of hydrocarbon groups in both FCC feeds and products. Aromatics were determined directly, and those saturated as a difference to 100%. (Table 3)

Table 3: Aromatic content in tested crudes and FCC products (NP HPLC/RID)

aromatic share, (% m/m)	FCC feed from REB crude	FCC gasoline from REB crude	LCU from REB crude	FCC feed from Syria Light crude	FCC gasoline from Syria Light crude	LCU from Syria Light crude
monoaromatics	17.7	28.1	17.1	14.8	23.9	23.6
diaromatics	8.5	0.7	54.5	5.0	0.7	51.4
tri+aromatics	10.4	0.1	2.1	9.7	-	1.0
polyaromatics	18.8	0.8	56.6	14.7	0.7	52.4
total aromatics	36.6	28.9	73.7	29.5	24.6	76.0

Saturated hydrocarbons are during the catalytic process turned into aromatic hydrocarbons and olefins, and, as a result, there is a considerable increase of aromatic compounds, especially semi-aromatics.

A certain reduction of the total aromatic content in lighter FCC fractions (FCC gasoline) was also observed, although the content of monoaromatics went up at the same time.

The generation of monoaromatics in FCC gasoline may be explained through the aromatization of cyclic components, oligomerization and conversion of saturated into naphthenic components.

The presence of naphthalenes in tri+ aromatic fraction may be explained by the less than perfect separation on the amino modified silica gel column, and the corrected position of the return valve.

Large aromatic content in light cyclic oil shows that this component may be used for blending into diesel fuel only with additional hydrotreatment.

Conclusion

By combining the shown results of gas and liquid chromatography, a more complete insight into the complex composition of FCC feeds and products has been achieved. The knowledge of individual and group composition of aromatic hydrocarbons in FCC feeds and fractions is important for the formulation of parameters of the FCC process itself, as well as the estimation of quality and environmental tolerability of the end commercial products.

By monitoring aromatic groups in light FCC products, it has been established that a reduction in the total aromatic content occured, with a simultaneous increase in the content of mono-aromatics, with regard to to the initial feed, while the aromatic content in cyclic oil increased at the same time. For the blending of cyclic oils into diesel fuels, consistent with the current quality requirements, additional treatment is needed.

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UDK	Ključne riječi:	Key words:
665.644.2	fluid katalitički kreking FCC	fluid catalytic cracking FCC
665.644.2.002.33	sirovine za FCC	raw materials for FCC
665.644.2.002.34	cirkulirajuće plinsko ulje FCC	FCC light cycle oil
665.6.033.25	osnovne sirovine prema sadržaju aromata	primary feeds according to aromatic constituents
665.733.5.033.25	sadržaj aromata u motornom benzinu	gasoline aromatic content
665.753.4.033.25	sadržaj aromata u dizelskom gorivu	diesel fuel aromatic content
665.7.035.7	ekološka prihvatljivost naftnih proizvoda	environmental acceptability of petroleum products

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