**Maja Fabulić Ruszkowski, Sanda Telen, Štefica Podolski, Tomislav Šarić**

# ISPITIVANJE RASPODJELE SUMPORA U TEKUĆIM PRODUKTIMA KREKIRANIH PLINSKIH ULJA

*Sažetak*

*Današnje sirovine za proces fluid katalitičkog krekiranja sadrže velike količine ostataka atmosferske i vakuum destilacije koje su bogate sumporom. Produkti nastali katalitičkim krekiranjem, prvenstveno FCC benzin i lako cikličko ulje, predstavljaju glavne izvore sumpora u motornom benzinu, odnosno dizelskom gorivu. FCC benzin sudjeluje s 35-40 vol %. u motornom benzinu, a pri tom daje 98 % od ukupnog sumpora prisutnog u motornim benzinima. Ove dvije činjenice ukazuju na važnost istraživanja raspodjele sumpora u FCC benzinu i drugim produktima katalitičkog krekiranja dobivenih iz različitih sirovina.*

*U radu su uspoređeni prinosi produkata katalitičkog krekiranja plinskih ulja dobivenih iz sirovina koje su sadržavale različite količine sumpora. Ispitivanja su provedena na laboratorijskom uređaju za katalitičko krekiranje pomoću testa mikroaktivnosti (MAT). Dobiveni tekući produkti krekiranja frakcionirani su te je dobivenim frakcijama benzina, lakog cikličkog ulja i dekantiranog ulja određen sadržaj sumpora. Frakcijama benzina određen je istraživački oktanski broj (IOB) koji je koreliran sa sastavom i raspodjelom ugljikovodika u benzinu te sa sadržajem sumpora u sirovini, tj. u benzinu.*

*Dobiveni rezultati pokazuju da korištenjem hidroobrađene sirovine dolazi do povećanja konverzije i prinosa FCC benzina, smanjenja IOB FCC benzina i smanjenja sadržaja sumpora u svim tekućim produktima krekiranja.*

## 1. UVOD

Jedan od najvećih izazova s kojim se susreću sve svjetske naftne kompanije je smanjenje zagađenja zraka koje nastaje emisijom štetnih tvari iz benzinskih motora. To se prvenstveno odnosi na smanjenje količine sumpora u motornim benzinima

budući da sumpor pored onečišćenja okoliša značajno smanjuje djelotvornost katalitičkih konvertera u automobilima. U tablici 1 prikazana je specifikacija sumpora u motornom benzinu u Europi i Sjevernoj Americi [1].

Tablica 1: Specifikacija sumpora u motornom benzinu
Table 1: The specification of sulphur in motor gasoline

| Svojstvo Properties | Sjeverna Amerika North America | | Europa | |
|---|---|---|---|---|
| | 2003 | EPA 2006 | 2003 | 2005 |
| Sumpor, mas. ppm Sulphur, wt% ppm | 330-340 | 30 | 150 maks. | 50 |

Mnoge europske vlade daju porezne olakšice naftnim kompanijama ako ranije započnu s primjenom specifikacije za 2005. godinu. Neke zemlje poput Njemačke i Velike Britanije već primjenjuju motorni benzin sa samo 10 ppm sumpora, odnosno 50 ppm [2]. Zakonodavstvo Europe i SAD-a nakon 2006. godine tražit će smanjenje sumpora na manje od 10 mas. ppm u benzinskom poolu, što predstavlja razinu koju rafinerije teško mogu dostići bez značajnih ulaganja.

Za razliku od zemalja EU, u Hrvatskoj se razina sumpora u motornim gorivima trenutačno kreće od 1000 ppm u motornom benzinu, do 5000 ppm, tj. 350 ppm za dizelsko gorivo, odnosno Eurodizel [3].

Kako u dimnim plinovima s FCC jedinica izlaze i velike količine $SO_X$ plinova, u nekim industrijski razvijenim područjima postoje ograničenja vezana uz emisiju $SO_X$ plinova koja su stroža od ograničenja vezanih za kvalitetu motornih goriva. Na snagu su stupile i stroge specifikacije vezane za smanjenje količine sumpora u dizelskom gorivu te loživom ulju. Glavnina sumpora, čak 98%, u sastavu motornog benzina dolazi upravo od FCC benzina, dok FCC benzin sudjeluje s približno 35-40 vol. % u sastavu motornog benzina [4]. Iz navedenih podataka uočava se važnost različitih tehnologija uklanjanja sumpora iz sirovine za FCC proces ili iz FCC benzina.
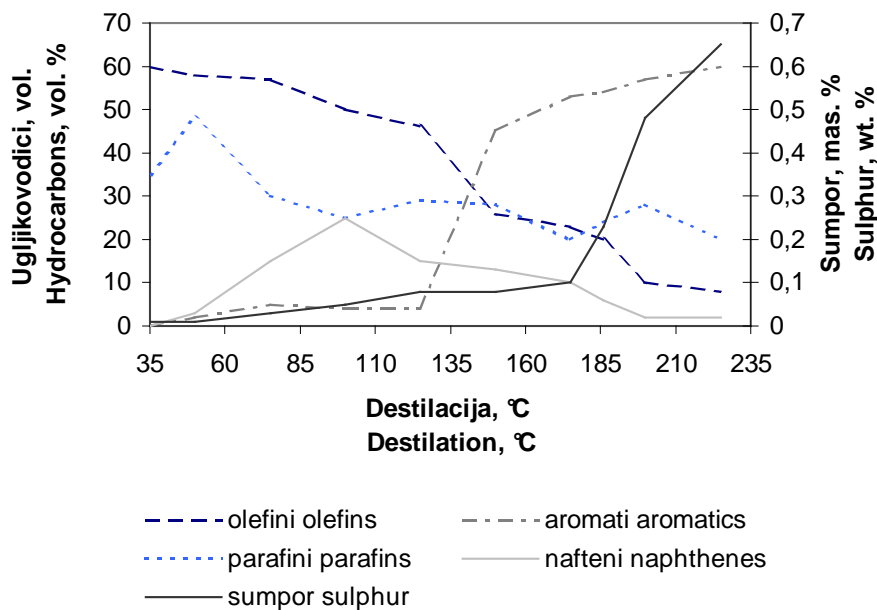
## 1.1 Načini uklanjanja sumpora iz FCC benzina

Izborom nafte može se najjednostavnije utjecati na količinu sumpora u produktima FCC procesa. Međutim, niskosumporne nafte vrlo su skupe na tržištu te je ova varijanta neprihvatljiva za rafinerije temeljene na FCC kao glavnom konverzijskom procesu. Pomoću ove opcije nije moguće smanjiti količinu sumpora u motornom benzinu na 50 mas. % ppm.

Dvije su osnovne tehnologije uklanjanja sumpora u produktima FCC procesa: obrada FCC sirovine ili obrada produkata dobivenih katalitičkim krekiranjem. Obrada FCC sirovine ili predtretman smatra se najučinkovitijom metodom uklanjanja sumpora i u produktima krekiranja i u dimnim plinovima, ali i najskupljom opcijom. Trošak predtretmana iznosi od 1,500-2,500 $ po barelu sirovine [1]. Prednost ove tehnologije je u tome da se povećava kovnerzija i prinos FCC benzina, a količina

sumpora se smanjuje i u dizelskom gorivu. Povećanje konverzije u FCC procesu dovodi do povećanja rafinerijske dobiti, dok se istovremeno smanjuju prinosi koksa, lakog cikličkog ulja i teškog cikličkog ulja [5,6]. Postrojenja za predobradu mogu raditi na dva načina: kao postrojenja za hidrodesulfurizaciju ili kao postrojenja za hidrokrekiranje. U oba procesa se pored reakcija desulfurizacije simultano odvijaju i reakcije denitrifikacije, deoksigenacije, demetalizacije, dearomatizacije i zasićenja olefina. Procesom hidrodesulfurizacije prvenstveno se obrađuju plinska ulja iz kojih se uklanja sumpor, a u cilju proizvodnje dizelskog goriva, dok se procesom hidrokrekiranja obrađuje sirovina za FCC proces. Proces hidrokrekiranja odvija se pri znatno višim tlakovima od procesa hidrodesulfurizacije.

Proces obrade produkata katalitičkog krekiranja predstavlja jednostavniju i jeftiniju tehnologiju kod koje ne nastaju viši prinosi željenih produkata u odnosu na tehnologiju predobrade sirovine. FCC benzin se pritom rasfrakcionira u laku i tešku frakciju. Laka frakcija obrađuje se na Merox postrojenju, dok se teška frakcija obrađuje procesima hidroobrade, kao što je npr. ISAL proces. Osim hidroobrade, u ISAL procesu odvijaju se i reakcije izomerizacije, ciklizacije i dealkilacije. Na taj način postiže se smanjenje sumpora, dok se oktanski broj ne mijenja ili se čak poveća [6].

Slika 1: Raspodjela količine sumpora i ugljikovodika pri destilaciji FCC benzina
Figure 1: FCC gasoline cumulative sulphur and hydrocarbon distibution

Najveća količina sumpora u FCC benzinu nalazi se u najtežoj destilacijskoj frakciji benzina koja čini zadnjih 15-20 vol. % (slika 1). Promjenom destilacijske granice FCC benzina, tj. uklanjanjem dijela najteže frakcije FCC benzina značajno se može smanjiti količina sumpora u FCC benzinu, ali i količina aromata koja će po specifikaciji za 2005. godinu iznositi najviše 35 vol. %. Metodom promjene destilacijske granice FCC benzina smanjuje se količina prinosa benzina, povećava prinos LCU te se problem sumpora rješava samo u FCC benzinu. U literaturi se navodi da se smanjenjem završne točke destilacije benzina s 221 °C na 204 °C (približno 8-10 vol. %) sadržaj sumpora reducira za 35-40 % [7].

## 1.2 Uloga aditiva i katalizatora za uklanjanje sumpora

Razvoj FCC katalitičkih sustava za smanjenje količine sumpora zahtijeva dobro razumijevanje i poznavanje kinetike sumpornih spojeva u benzinu. Danas na tržištu postoje specijalno dizajnirani katalizatori i aditivi za smanjenje količine sumpora u produktima katalitičkog krekiranja. Iako je uporabom aditiva i katalizatora za smanjenje sumpora količina sumpora u FCC benzinu u pojedinim slučajevima smanjena i do 20 % [8], sama uporaba katalizatora, odnosno aditiva nije dostatna da se postigne specifikacija od 50 ppm sumpora u motornom benzinu 2005. godine.

## 1.3 Raspodjela sumpora u produktima katalitičkog krekiranja

Današnje sirovine za proces fluid katalitičkog krekiranja sadrže velike količine ostataka atmosferske i vakuum destilacije koje su bogate sumporom i ostalim kontaminantima. Produkti nastali katalitičkim krekiranjem, prvenstveno FCC benzin i lako cikličko ulje predstavljaju glavne izvore sumpora u motornom benzinu, odnosno dizelskom gorivu.

Iako desulfurizacija nije primarni cilj operacija katalitičkog krekiranja, čak i do 50% sumpora konvertira se u $H_2S$ tijekom FCC procesa. $H_2S$ nastaje katalitičkom dekompozicijom netiofenskih sumpornih spojeva (neprstenastih spojeva). Poznato je da u produktima katalitičkog krekiranja sadržaj sumpora može varirati od 15-70 mas.%, ovisno o korištenoj sirovini, tipu katalizatora i procesnim uvjetima.

Općenito vrijedi da se veći dio sumpora iz tekućeg produkta krekiranja raspodijeli u ciklička ulja, a manji dio u benzin i koks na katalizatoru [9]. U cikličkim uljima i ostatku prevladavaju aromatski sumporni spojevi – tiofeni koji se kao i aromatski spojevi teško krekiraju te uzrokuju postizanje niže konverzije [10]. Raspodjela sumpora kod hidrotretirane sirovine drukačija je od raspodjele sumpora kod nehidrotretirane sirovine.

# 2. EKSPERIMENTALNI DIO

## 2.1. Katalizatori i sirovine

Sve sirovine testirane su ravnotežnim uzorkom katalizatora A koji se koristio u RN Rijeka. Korišteni katalizator odlikuje se poboljšanim prinosom benzina te

poboljšanom koksnom i plinskom selektivnošću u odnosu na prije korištene katalizatore od istog proizvođača. On također minimizira dehidrogenacijsku aktivnost kontaminanata poput nikla i vanadija te smanjuje sumpor u benzinu u odnosu na dosad korištene REUSY katalizatore. U tablici 2 dana su svojstva korištenog katalizatora.

Tablica 2: Fizikalno-kemijska svojstva svježeg korištenog katalizatora
Table 2: Physical and chemical properties of fresh used catalyst

| $Al_2O_3$, mas. % | 43,0 |
|---|---|
| $Na_2O_3$, mas. % | 0,3 |
| $Re_2O_3$, mas. % | 2,7 |
| Specifična površina, $m^2\ g^{-1}$<br>Surface Area, | 280 |
| Volumen pora, $ml\ g^{-1}$<br>Pore Volume | 0,40 |
| Nasipna gustoća, $g\ ml^{-1}$<br>Apparent bulk density | 0,73 |
| Raspodjela veličina čestica, mas. %<br>Partical Size Distribution | |
| 0-20 μm | 1 |
| 0-40 μm | 15 |
| 0-80 μm | 60 |
| 0-149 μm | 92 |
| prosječna raspodjela, μm<br>Average Particle Size | 70 |

Korištene su: FCC sirovina iz RN Rijeka koja je hidrodesulfurizirana na poluindustrijskom postrojenju za obradu hidroobradu u Sektoru strateškog razvoja, istraživanja i investicija (sirovina 1), standardna sirovina iz RN Sisak koja se koristi za MAT testiranje (sirovina 2) i nedesulfurizirana FCC sirovina iz RN Rijeka (sirovina 3). Sirovine 1 i 3 realne su sirovine koje se koriste u RN Rijeka kao sirovine za FCC postrojenje. Sirovina 1 je hidrodesulfurizirana kod sljedećih uvjeta: temperatura reaktora=380 °C, tlak reaktora=40 bar, omjer vodik/ sirovina=100, prostorna brzina (LHSV)=1,00 $h^{-1}$. U tablici 3 navedena su fizikalno-kemijska svojstva korištenih sirovina.

Iz fizikalno-kemijskih svojstava (tablica 3) uočava se da se sirovina 1 (hidrodesulfurizirana sirovina iz RN Rijeka) najlakše krekira jer sadrži najviše dugolančanih parafinskih ugljikovodika. To se vidi iz podataka n-d-M analize (%$C_P$=71,60) te karakterističnog faktora K=12,40 koji upućuje da se radi o parafinskoj sirovini. Ova sirovina ujedno ima najmanju količinu sumpora i najnižu temperaturu vrenja. Sirovina 2 (standardna sirovina iz RN Siska) sadrži gotovo

jednaku količinu aromatskih i naftenskih ugljikovodika, a po K faktoru može se klasificirati kao naftenska sirovina s nešto višim °API od nedesulfurizirane sirovine te nižom točkom završetka vrenja ASTM destilacije. Nedesulfurizirana sirovina (sirovina 3) sadrži najviše naftenskih ugljikovodika (%$C_N$=18,64), ima najnižu vrijednost °API, najviši raspon temperatura vrenja, najvišu Mn i gustoću te najvišu količinu sumpora.

Tablica 3: Fizikalno-kemijske karakteristike korištenih sirovina
Table 3: Physical and chemical properties of feedstock

| SVOJSTVO<br><br>PROPERTIES | METODE<br><br>METHOD | HDS. FCC SIROVINA IZ RN RIJEKA<br>(sirovina 1)<br>(feedstock 1) | STAND. SIROVINA IZ RN SISAK<br>(sirovina 2)<br>(feedstock 2) | NEDESULFURUZIRANA FCC SIROVINA IZ RN RIJEKA<br>(sirovina 3)<br>(feedstock 3) |
|---|---|---|---|---|
| Gustoća, 15 °C,<br>Density, 15 °C, kgdm$^{-3}$ | ASTM D 1298 | 0,867 | 0,8847 | 0,8906 |
| ° API | ASTM D 287 | 30,92 | 28,36 | 27,30 |
| ASTM destilacija,<br>ASTM destillation | | ASTM D 2887 | ASTM D 1160 | ASTM D 1160 |
| Početak, °C    IBP, °C | | 189,1 | 223,5 | 211,3 |
| 10 % v/v | | 271,1 | 332,6 | 295,7 |
| 50 % v/v | | 369,2 | 413,0 | 411,0 |
| 90 % v/v | | 462,1 | 491,4 | 514,2 |
| 95 % v/v | | 484,9 | 510,9 | 538,4 |
| Sumpor,<br>Sulphur, % m/m | ASTM D 4294 | 0,0280 | 0,52 | 1,27 |
| Viskoznost,<br>Viscosity mm²/s,  40 °C<br>           100 °C | ASTM D 445 | 10,36<br>2,80 | 23,34<br>4,44 | 21,92<br>4,15 |
| Tecište,<br>Pour point, °C | ASTM D 97 | +30 | +39 | +33 |
| Indeks loma,<br>Refractive index, 70 °C | ASTM D 1747 | 1,4892<br>(na 20°C) | 1,4749 | 1,47626 |
| Srednja molekulska masa<br>Average molecular mass | ASTM D 2502 | 326 | 377 | 408 |
| Karakteristični faktor<br>K factor | UOP 375 | 12,40 | 12,10 | 11,98 |
| n-d-M analiza.<br>n-d-M analysis, % $C_{Až}$ | ASTM D 3238 | 20,94 | 15,50 | 13,65 |
| % $C_N$ | | 7,46 | 17,58 | 18,64 |
| % $C_P$ | | 71,60 | 66,92 | 67,91 |
| $R_A$ | | 0,85 | 0,70 | 0,67 |
| $R_N$ | | 0,31 | 0,85 | 1,16 |

## 2.2 Metode

Ispitivanja sirovina provedena su na laboratorijskom uređaju za katalitičko krekiranje pomoću testa mikroaktivnosti (eng. micro activity test, MAT) po modificiranoj ASTM D 3907 metodi u cijevnom reaktoru s nepokretnim slojem katalizatora.

Eksperimentalni uvjeti primijenjeni pri katalitičkom krekiranju na MAT-aparaturi prikazani su u tablici 4.

Tablica 4: Uvjeti testiranja na MAT aparaturi
Table 4: Testing conditions applied in the MAT-aparatus

| | |
|---|---|
| Masa katalizatora,<br>Mass of catalyst, g | 4,000· |
| Omjer C/O<br>Cat./oil ratio | 3,01 |
| Prostorna brzina,<br>Space velocity, $h^{-1}$ | 15,96 |
| Masa dozirane sirovine,<br>Mass of injection feedstock, g | 1,3300· |
| Temperatura reakcije,<br>Reaction temperature, °C | 482, 520, 530, 540 |
| Temperatura regeneracije,<br>Regeneration temperature, °C | 650 |
| Temperatura predgrijavanja sirovine,<br>Feedstock preheat temperature, °C | 60 |
| Vrijeme stripiranja ugljikovodika s katalizatora,<br>Time of stripping hydrocarbon from catalyst, s | 900 |
| Vrijeme kontakta sirovine i katalizatora,<br>Time of contact feedstock and catalyst, s | 75 |
| Vrijeme regeneracije,<br>Regeneration time, s | 2800 (zrak/air) + 1000 ($N_2$) |

Na osnovi eksperimentalnih podataka dobivenih kromatografskom metodom simulacijske destilacije izračunati su prinosi pojedinih komponenti tekućeg produkta. Frakcioniranjem tekućeg produkta na mikrofrakcionatoru dobivena je frakcija kreking benzina te frakcija lakog i teškog cikličkog ulja. Ugljikovodični sastav kreking benzina određen je metodom plinske kromatografije visokog razlučivanja. IOB benzina izračunat je na osnovi ugljikovodičnog sastava određenog plinskom kromatografijom pomoću interne metode koju je razvio Laboratorij za plinsku kromatografiju, INA, Sektor strateškog istraživanja i investicija [11]. Sadržaj sumpora u tekućim produktima krekiranja određen je po HRN ISO 8754 metodi za određivanje sumpora u naftnim produktima pomoću disperzije X-zraka na energo-disperznom fluorescentnom spektrometru.

# 3. REZULTATI I RASPRAVA

## 3.1 Određivanje raspodjele produkata katalitičkog krekiranja

Ispitana je ovisnost konverzije katalitičkog krekiranja i prinos frakcija benzina o temperaturi krekiranja (slika 2 i 3). Porast temperature uvjetovao je porast konverzije pri čemu je najviše vrijednosti konverzije postigla sirovina 1. Sirovina 1 je hidrodesulfurizirana sirovina parafinskog tipa, izrazito podložna krekiranju što se vidi iz njezinih fizikalno-kemijskih karakteristika (tablica 3). U procesu hidro-desulfurizacije dolazi do povećanja količine parafinskih ugljikovodika koji nastaju zasićenjem olefinskih ugljikovodika.

Porastom temperature do 540°C dolazi do porasta pri nosa FCC benzina. Najviši prinos benzina postignut je uz sirovinu 1. Povećani prinos benzina bilježi se kod hidrodesulfuriziranih sirovina zbog povećane krekibilnosti sirovine te smanjenja količine lakog cikličkog ulja, teškog cikličkog ulja i koksa. Prinosi benzina na temperaturi od 540°C, tj. iznad 75 mas. % konverzij e počinju padati pri korištenju sirovine 1 i 3 jer dolazi do prekrekiranja benzina. Korištenjem sirovine 2 ostvarene su niže vrijednosti konverzije od 75 mas. % te nije došlo do prekrekiranja.
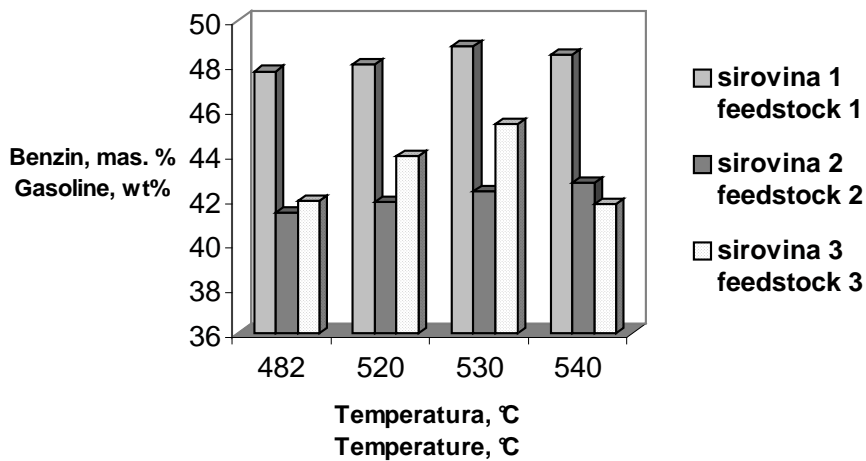
Slika 2: Ovisnost konverzije o temperaturi krekiranja
Figure 2: Dependence of conversion on cracking temperature
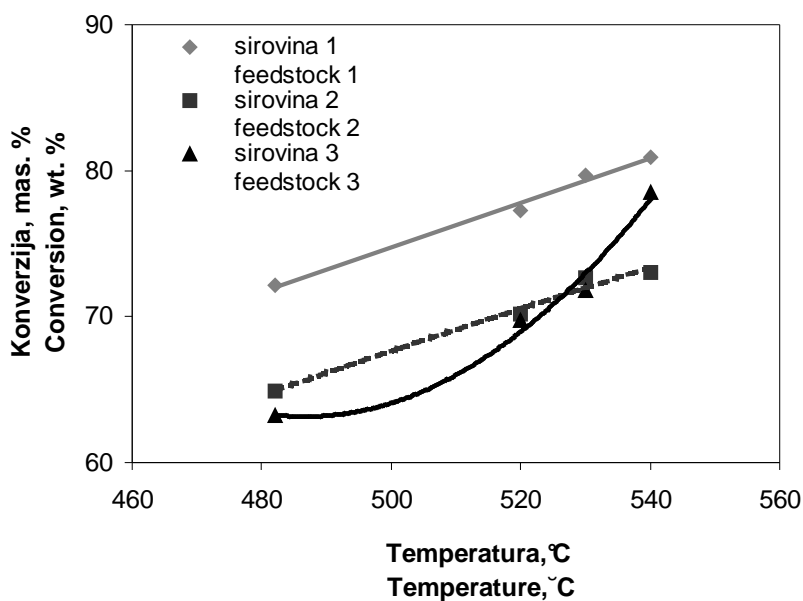
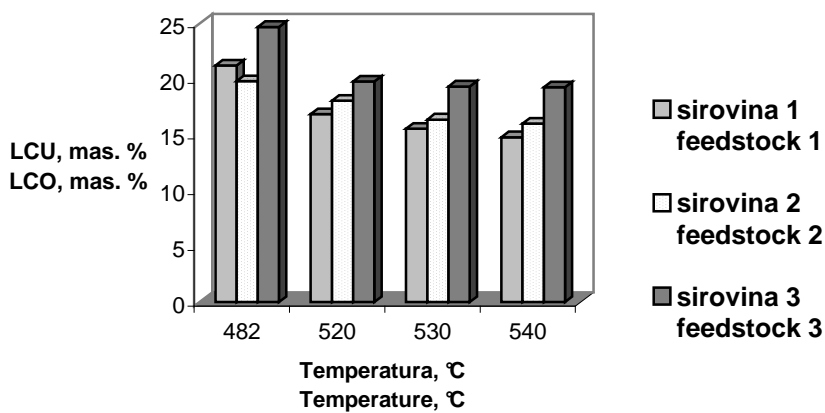Slika 3.:Ovisnost prinosa benzina o temperaturi
Figure 3: Dependence of gasoline yield on cracikg temperature



Slika 4: Ovisnost prinosa LCU o temperaturi krekiranja
Figure 4: Dependence of LCO yield on cracking temperature

Prinos lakog cikličkog ulja LCU smanjuje se s porastom temperature (slika 4). Korištenjem sirovina 3 (nehidrodesulfurizirana sirovina) postignut je najviši prinos lakog cikličkog ulja (LCU).

## 3.2 Određivanje raspodjele sumpora u produktima katalitičkog krekiranja

FCC sirovina obično sadrži 0,3-3,0 mas. % sumpora u različitim spojevima poput merkaptana, sulfida, disulfida i tiofena. Iz netiofenskih spojeva uglavnom nastaje $H_2S$, dok u tekućim produktima prevladavaju tiofenski spojevi sumpora koji se teško krekiraju.

U radu se odredio sadržaj sumpora u benzinu, lakog cikličkog ulja (LCU) i dekantiranog ulja (DU) dobivenim iz sirovina s različitim sadržajem sumpora. U tablici 5 prikazana je raspodjela sumpora iz sirovina u svim produktima krekiranja.

Tablica 5: Raspodjela sumpora u produktima krekiranja
Table 5: Sulphur distibution in cracking products

| sirovina feedstock | sirovina, feedstock, ppm | Količina ukupnog sumpora, The quantity of total sulphur, % | | | | |
|---|---|---|---|---|---|---|
| | | $H_2S$ + koks* $H_2S$ + coke* | tekuć.produkt liquid product | benzin gasoline | LCU | DU |
| 1 | 280 | 51,8 | 48,2 | 7,1 | 23,2 | 17,9 |
| 2 | 5200 | 53,9 | 46,1 | 9,6 | 19,2 | 17,3 |
| 3 | 12700 | 56,7 | 43,3 | 11,0 | 17,3 | 15,0 |

*Količina sumpora u dimnom plinu u obliku $H_2S$ i u koksu dobivena je računski.
*The quantity of sulphur in flue gas in the form of $H_2S$ and in the coke is mathematicaly determined.

U tablici 5 se vidi da se veća količina sumpora raspoređuje u ciklička ulja (lako cikličko ulje 17-23% i dekantirano ulje 15-18 %), dok se manja količina raspoređuje u benzin (7-11%).

Sadržaj sumpora u benzinu nastalom iz nehidrodesulfuriziranih sirovina 2 i 3 viši je od onog iz hidroobrađene siroivine 1. Sirovina 1 sadrži višu količinu sumpora raspoređenu u CU i DU od nehidroobrađenih sirovina [12].

Dobiveni rezulati raspodjele sumpora u tekućim produktima u skladu su s rezultatima dobivenim s poluindustrijskog postrojenja gdje je iznos količine sumpora u tekućem produktu kod nehidrodesulfuriziranih plinskih ulja iznosio 45 ± 5 mas. % sumpora [13].

Količina sumpora iz koje nastaje $H_2S$ te količina sumpora na koksu nije se mogla odrediti eksperimentalno.

Kod nehidrodesulfuriziranih sirovina visok postotak sumpora prisutan je u obliku $H_2S$ (50 ± 10 mas. %) koji sadrži uglavnom netiofenske spojeve[13]. Hidroobrađena sirovina sadrži uglavnom visoki postotak tiofenskih spojeva, jer za vrijeme reakcije hidroobrade dolazi do uklanjanja netiofenskih spojeva.

Kod nehidrotretiranih sirovina količina sumpora u benzinu predstavlja  ~ 10 % ukupne količine sumpora prisutne u sirovini, dok je kod hidrotretirane sirovine količina sumpora manja te iznosi 5-7 % ukupne količine sumpora [10].

Sumpor sadržan na koksu koji se nalazi na katalizatoru izvor je emisije sumpornih oksida u FCC jedinici. Izgaranjem koksa na katalizatoru u tijeku regeneracije sumpor oksidira u $SO_x$. Količina nastalih $SO_x$ ovisi o tipu sumpornih spojeva u sirovini i prinosu koksa. Literaturni izvori navode različite podatke za količinu sumpora na koksu. Tako podatak dobiven iz poluindustrijskog postrojenja navodi da se količina sumpora na koksu kod nehidrodesulfuriziranih sirovina kreće 7 ± 4 mas. % [14], dok se spominje i podatak kod kojeg količina sumpora može biti čak i do 28 mas. % od ukupne količine sumpora u sirovini [13].

## 3.3 Određivanje ugljikovodičnog sastava i IOB frakcije benzina

Na slici 5 prikazana je raspodjela ugljikovodika u frakciji benzina, dok je na slici 6 prikazana ovisnost IOB o količini sumpora u benzinu.

Slika 5: Raspodjela ugljikovodika u benzinu
Figure 5: Distibution of hydrocarbons in gasoline
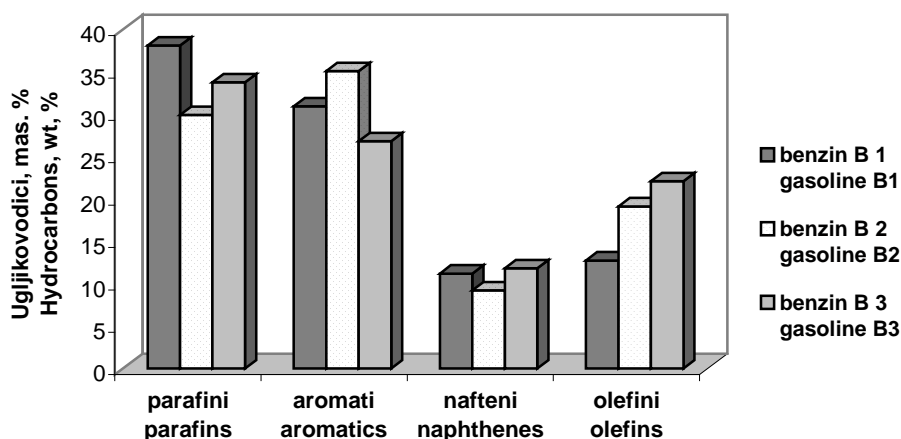
Aromatski i olefinski ugljikovodici imaju najviše vrijednosti oktanskog broja. Benzin B 1 dobiven iz sirovine 1 ima najviše parafinskih ugljikovika (n-parafina i izo-parafina) te najmanje olefinskih ugljikovodika te je ostvario najniži IOB (IOB=91,9). Benzin B 2 dobiven iz sirovine 2 ima najviše aromatskih ugljikovodika i srednji IOB u odnosu na ostale benzine (IOB=92,4). Benzin B 3 ima najviše naftenskih i olefinskih ugljikovodika te najviši IOB (IOB=92,8).

Benzin s manjom količinom aromatskih i olefinskih uglljikovdika, tj. s manjom količinom aromatskih sumpornih spojeva ostvaruje niži oktanski broj. Smanjenje oktanskih brojeva u FCC benzinu do kojeg dolazi hidroobradom sirovine može se regulirati kontrolom procesnih parametara. Poželjno je FCC proces voditi na taj način da se smanji temperatura reakcije te se na taj način favoriziraju reakcije izomerizacije koje dovode do nastajanja izospojeva s visokim oktanskim brojem. Oktanski broj u komercijalnim motornim benzinima podiže se dodavanjem visokooktanskih komponenti poput oksigenata, izomerizata, alkilata i reformata [14, 15].

Benzin B 1 dobiven iz hidrodesulfurizirane sirovine 1 po količini sumpora jedini bi zadovoljio trenutačnu europsku specifikaciju motornih benzina što ukazuje na nužnost hidroobrade sirovine.

Slika 6: Ovisnost IOB o količini sumpora u benzinu
Figure 6: Dependence of RON on sulphur in gasoline
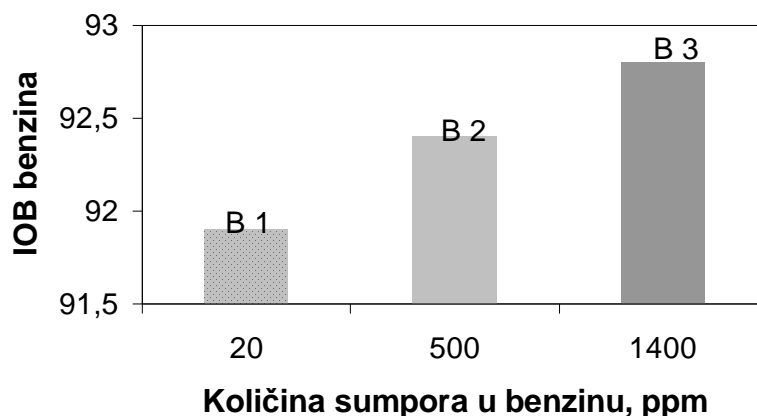
# 4. ZAKLJUČCI

1. Najviša konverzija postignuta je korištenjem hidroobrađene sirovine. U procesu hidrodesulfurizacije došlo je do povećanja udjela parafinskih ugljikovodika iz naftenskih ugljikovodika u sirovini što je znatno povećalo njezinu sklonost krekiranju.

2. Katalitičkim krekiranjem hidrodesulfurizirana sirovina ostvarila je veći prinos benzina za 3,5 - 6,7 mas. % od nehidrodesulfuriziranih sirovina, dok je kod sve tri sirovine zapaženo smanjenje prinosa lakog cikličkog ulja (LCU).

3. Sadržaj sumpora u benzinu nastalom iz hidrodesulfurizirane sirovine niži je od sadržaja sumpora u benzinu nastalog iz nehidroobrađenih sirovina. Također je kod iste sirovine kod raspodjele sumpora u tekućim produktima zapažen viši udio sumpora u lakom cikličkom ulju (LCU) i dekantiranom ulju (DU) te manji udio sumpora u benzinu.

4. Smanjenje oktanskog broja vezano uz smanjenje količine sumpora u FCC benzinu nastoji se ublažiti usmjeravanjem FCC procesa k proizvodnji benzina s većim sadržajem izospojeva, dok se manjak oktanskih brojeva u poolu motornih benzina nadoknađuje dodatkom izomerizata, alkilata i oksigenata.

5. Iz rezultata dobivenih ovim ispitivanjem vidljivo je da benzin dobiven iz hidrodesulfurizirane sirovine 1 po količini sumpora jedini zadovoljava trenutačnu specifikaciju motornih benzina, što ukazuje na nužnost hidroobrade sirovine za FCC proces.

# TESTING SULPHUR DISTRIBUTION IN LIQUID PRODUCTS OF CRACKED GAS OILS

*Abstract*

*The present feeds for the fluid catalytic cracking process contain large residual quantities of atmospheric and vacuum distillations that are rich in sulphur. The catalytic cracking products, primarily the FCC gasoline and light cyclic oil, represent the main sources of sulphur in motor gasoline and diesel fuel. The FCC gasoline share is 40 vol.% in motor gasoline, and it provides 98% of the total sulphur quantity contained in motor gasoline. These two facts emphasize the importance of testing sulphur distribution in FCC gasoline and in other products of catalytic cracking obtained from various feeds.*

*The paper compares the yields of gas oil catalytic cracking products obtained from the feeds containing different quantities of sulphur. Tests have been performed on the laboratory device for catalytic cracking by means of a microactivity test (MAT). The obtained liquid products of cracking are fractionated, so that the resulting fractions of gasoline, light cyclic oil and heavy cyclic oil have a determined sulphur content. The research octane number (RON) has been determined for gasoline fractions, and correlated with the content and distribution of hydrocarbons in gasoline, as well as with the content of sulphur in the feed i.e. gasoline.*

*The obtained results show that by using hydrotreated feed the conversion and yield of FCC gasoline have increased, while FCC gasoline RON has decreased, as well as the content of sulphur in gasoline and other liquid products of cracking.*

## 1. INTRODUCTION

One among the greatest challenges with which all global oil companies are faced is the reduction of air pollution caused by the emission of harmful substances from gasoline engines. This primarily refers to the reduction of sulphur volume in motor gasolines since sulphur not only causes environmental pollution but also considerably reduces the efficiency of catalytic converters in automobiles. Table 1 shows sulphur specification in motor gasoline in Europe and North America [1].

Many European governments allow tax relaxations to oil companies if they start earlier with the application of the specification for 2005. Some countries, like Germany and Great Britain, are already applying motor gasoline with only 10, i.e. 50

ppm of sulphur [2]. The legislation of Europe and the USA shall beyond 2006 require sulphur reduction to less than 10 mas. ppm in the gasoline pool, which is a level that the refineries will find hard to reach without major investments.

Unlike the EU countries the sulphur level in motor gasoline in Croatia is currently ranging from 1000 ppm in motor gasoline to 5000 ppm, i.e. over 350 for diesel fuel i.e. Eurodiesel[3].

Since flue gases of the FCC units contain also large volumes of $SO_X$ gases, in some industrially developed areas there are limitations as to the emission of $SO_X$ gases which are more stringent than those associated with motor fuel quality. In force are also stringent specifications associated with the reduction of sulphur content in diesel fuel and fuel oil. Most sulphur in motor gasoline, as much as 98%, comes from FCC gasoline, while FCC gasoline has an aproximately 35 vol.% share in the composition of motor gasoline [4]. The said data point to the importance of various technologies of removing sulphur from the FCC process feed or from the FCC gasoline.

## 1.1 The Ways of Removing Sulphur from FCC Gasoline

Feed selection constitutes the simplest way of impacting sulphur volume in FCC process products. However, low sulphur feeds are very expensive on the market, which is why this variant is unacceptable for refineries based on FCC as the main conversion process. This option cannot reduce the sulphur volume in motor gasoline down to 50 mas. % ppm.

There are two basic technologies of sulphur removal from FCC process products: treatment of FCC feed or treatment of products obtained by catalytic cracking. Treatment of the FCC feed or pretreatment is considered to be the most efficient method of sulphur removal in both cracking products and flue gases, but also the most expensive one. The pretreatment cost is from 1,500-2,500 $ per feed barrel [1]. The advantage of this technology lies in the fact that FCC gasoline conversion and yield increase, while the sulphur content is reduced in diesel fuel as well. Increased conversion in FCC process leads to higher refinery profit, while at the same time reducing the yields of coke, light cyclic oil and heavy cyclic oil [5,6].

The pretreatment plants may operate in the following two ways: as hydrodesulphurization or as hydrocracking plants. In both processes the desulphurization reaction is accompanied by denitrification, deoxigenation, demetalization, dearomatization and olefin saturation. The hydrodesulphurization process primarily treats gas oils from which sulphur is being removed, for the purpose of producing diesel fuel, while hydrocracking process treats the FCC process feed. The hydrocracking process takes place at much higher pressures than the hydrodesulphurization process.

The process of treating catalytic cracking products constitutes a simpler and cheaper technology for refineries without higher yields of desired products with regard to the feed pretreatment technology. FCC gasoline is fractionated into light

and heavy fraction. Light fraction is treated in the Merox plant, while the heavy one is treated by hydrotreatment processes, such as, for example, the ISAL process. Apart from hydrotreatment, the ISAL process includes also the reactions of isomerization, cyclization and dealkylation. Sulphur reduction is thus achieved, while the octane number does not change or even increases [6].

The highest amount of sulphur in FCC gasoline is in the heaviest distillation gasoline fraction making the last 15-20 vol. % (Figure 1). By changing the distillation limit of FCC gasoline i.e. by removing a part of the heaviest fraction of FCC gasoline, one may considerably reduce the FCC gasoline sulphur content, but also the aromatic content, which will-according to the specification for 2005 amount to max. 35 vol.%. The use of the method of changing the FCC gasoline distillation limit reduces the volume of gasoline yield, increases LCO yield, and resolves the problem of sulphur only in FCC gasoline. The references state that by changing the gasoline end distillation point from 221 °C to 204 °C (approxima tely 8-10 vol %) sulphur content is reduced by 35-40 % [7].

## 1.2 The Role of Additives and Catalysts in Sulphur Removal

Development of FCC catalytic systems for reducing sulphur volume requires a good understanding and knowledge of the gasoline sulphur compounds kinetics. Available today on the market are specially designed catalysts and additives for reducing sulphur volume in catalytic cracking products. Although the use of additives and catalysts for sulphur reduction managed to reduce the FCC gasoline sulphur content in some cases up to 20 % [8], the use of catalysts i.e. additives itself is not sufficient for achieving the 2005 specification of 50 ppm sulphur in motor gasoline.

## 1.3 Sulphur Distribution in Catalytic Cracking Products

Today's feeds for the fluid catalytic cracking process contain large volumes of atmospheric and vacuum distillation residues rich in sulphur and other contaminants. Products obtained by catalytic cracking, primarily FCC gasoline and light cyclic oil, constitute the main sulphur sources in motor gasoline, i.e. diesel fuel.

Although desulphurization is not the primary goal of catalytic cracking operations, as much as up to 50 % of sulphur is converted to $H_2S$ in the FCC process. $H_2S$ is created through catalytic decomposition of non-tiophene sulphur compounds (non-ring compounds). It is known that in catalytic cracking products sulphur content may vary from 15-70 mas %, depending on the feed used, catalyst type and process conditions.

Usually, the largest part of sulphur from the fluid cracking product is distributed into cyclic oils, and a smaller part into the gasoline and coke on the catalyst [9]. In cyclic oils and residue aromatic sulphur compounds – tiophenes prevail, which are, as aromatic compounds, heavy to crack and cause lower conversion [10]. Sulphur distribution in hydrotreated feed is different than that in the non-hydrotreated one.

# 2. THE EXPERIMENTAL PART

## 2.1. Catalysts and Feeds

All the feeds were tested with a balanced catalyst sample A used in the Rijeka Oil Refinery. The catalyst used is characterized by improved gasoline yield and improved coke and gas selectivity with regard to the catalysts used previously by the same manufacturer. It also minimizes dehydrogenation activity of contaminants such as nickel and vanadium, while at the same time reducing the gasoline sulphur content with regard to the so far used REUSY catalysts. Table 2. specifies properties of the catalyst used.

Used were the FCC feed from the Rijeka Oil Refinery hydrodesulphurized on a semi-industrial plant Andreas Hoffer in SSRII (feedstock 1), standard feed from the Sisak Oil Refinery used for microactivity testing MAT (feedstock 2) and non-desulphurized FCC feed from the Rijeka Oil Refinery ( feedstock 3). Feedstocks 1 and 3 are real feeds used in Rijeka refinery as FCC plant feeds. Feedstock 1 has been hydrodesulphurized under the following conditions: reactor temperature = 380°C, reactor pressure = 40 bar, hydrogen/feedstock ratio = 100, spatial velocity (LHSV = 1,00 h$^{-1}$. Table 3 brings the physico-chemical properties of the feedstocks used.

The physico-chemical properties (Table 3) reveal that feedstock 1 (hydro-desulphurized feedstock from Rijeka refinery) is most easily cracked because it contains most long-chained paraffinic hydrocarbons. This may be seen from the data of n-d-M analysis (%$C_P$ = 71.60) and K factor K=12.40 revealing that it is a paraffinic feedstock. This feedstock also has the lowest sulphur content and the lowest boiling temperature. Feedstock 2 (standard feedstock from Sisak Refinery) contains an almost equal volume of aromatic and naphthenic hydrocarbons, while – according to its K factor, it may be classified as a naphthenic feedstock with somewhat lower °API than the non-desulphurized feed stock and lower end ASTM distillation point. Non-desulphurized feedstock (feedstock 3) contains the most naphthenic hydrocarbons (%$C_N$=18,64), has the lowest °API value, the highest boiling temperature range, the highest Mn and density, and the highest sulphur content.

## 2.2 The Methods

Feedstock tests were performed on a laboratory device for catalytic cracking using the microactivity test (MAT), according to the modified ASTM D 3907 method in a pipe reactor with immovable catalyst layer. Experimental conditions used in catalytic cracking on MAT-device are shown in Table 4.

Based on experimental data obtained through chromatografphic method of simulated distillation, calculated were the yields of individual liquid product components. By fractionating the liquid product on the microfractionator obtained

was the cracking gasoline fraction and the light and heavy cyclic oil fraction. Hydrocarbon composition of cracking gasoline was determined using the high resolution gas chromatography method. Gasoline RON was calculated on the basis of hydrocarbon composition determined by gas chromatography using the internal method developed by the Gas Chromatography Laboratory, INA, SSRII [11]. Sulphur content in liquid cracking products was determined according to the HRN ISO 8754 method for sulphur determination in oil products using X-ray dispersion on an energy-dispersing XRFspectrometer.

# 3. RESULTS AND DISCUSSION

## 3.1 Determining the Catalytic Cracking Products Distribution

Tested was the dependence of catalytic cracking conversion and gasoline fractions yield on the cracking temperature (Figures 2 i 3). Temperature increase has conditioned conversion increase, with the highest conversion values achieved by feedstock 1. Feedstock 1 is a hydrodesulphurized feedstock of paraffinic type, extremely prone to cracking, as may be seen from its physico-chemical properties (Table 3). In the hydrodesulphurization process the volume of paraffinic hydrocarbons created through saturation of olefinic hydrocarbons increases.

Temperature increase up to 540 °C causes FCC gasoline yield increase. The highest gasoline yield was achieved with feedstock 1. Increased gasoline yield is recorded for hydrodesulphurized feedstocks with increased feed crackability and lowered light cyclic oil, heavy cyclic oil, and coke volume. Gasoline yields at the tememprature of 540 °C, i.e. above 75 mas. % of conv ersion begin decreasing while using feedstocks 1 and 3 because gasoline precracking occurs. By using feedstock 2, lower conversion values than 75 mas. % were achieved, which is why precracking did not occur.

LCO yield is reduced with temperature increase (Figure 4). By using feedstock 3, (non-desulphurized feedstock), the highest LCO yield was achieved.

## 3.2 Determining Sulphur Distribution in Catalytic Cracking Products

FCC feed usually contains 0.3-3.0 mas. % of sulphur in various compounds, such as mercaptane, sulphide, disulphide and tiophene. Non-tiophenic compounds mostly provide $H_2S$, while in the liquid products tiophenic sulphur compounds prevail, which are hard to crack.

The paper presents sulphur content determined in gasoline, LCO and HCO obtained from feeds with various sulphur content. Table 5 presents sulphur distribution from feeds in all cracking products.

It may be observed from Table 5 that a larger amount of sulphur is being distributed into cyclic oils (light cyclic oil 17-23 % and decanted oil 15-18 %), while a smaller volume is distributed into gasoline (7-11 %).

Sulphur content in gasoline obtained from non-desulphurized feeds 2 and 3 is higher than that of the hydrotreated feedstock 1. Feedstock 1 contains a higher sulphur volume distributed into LCO and HCO than non-hydrotreated feeds[12].

The obtained results of sulphur distribution in liquid products are consistent with the results obtained at the semi-industrial plant where the sulphur volume amount in the liquid product for non-hydrodesulphurized gas oils was $45 \pm 5$ mas. % of sulphur [13].

The volume of sulphur from which $H_2S$ is generated and that on the coke could not be determined experimentally.

For non-hydrodesulphurized feeds, the high percentage of sulphur is present in the form of $H_2S$ ($50 \pm 10$ mas. %), containing mostly non-tiophenic compounds [13]. Hydrotreated feedstock mostly contains a high percentage of tiophenic compounds, because, during the hydrotreatment reaction, the non-tiophenic compounds are being removed.

For non-hydrotreated feeds, the gasoline sulphur content constitutes ~ 10 % of total sulphur content in the feed, while in the hydrotreated feeds the sulphur level is lower and amounts to 5-7% of total sulphur volume[10].

Sulphur contained in the coke on the catalyst is the emission source of sulphur oxides in the FCC unit. Through coke combustion on the catalyst during regeneration, sulphur oxidizes into $SO_x$. The volume of generated $SO_x$ is dependent on the volume of sulphur compounds in the feed and on coke yield. References state different data for sulphur volume on the coke. Thus the data obtained from the semi-industrial plant state that the volume of sulphur on coke for non-hydrodesulphurized feeds ranges from $7 \pm 4$ mas. % [14], while it is also said that sulphur level may be up to as much as 28 mas. % of the total sulphur level in the feed [13].

## 3.3 Determination of Hydrocarbon Composition and Gasoline Fraction RON

Figure 5 presents hydrocarbons distribution in gasoline fraction, while Figure 6 shows RON dependence on gasoline sulphur content. Gasoline B 1 obtained from feedstock 1 has the most paraffinic hydrocarbons (n-paraffins and iso-paraffins) and the least olefinic hyrdrocarbons resulting in the lowest RON (RON=91.9). Gasoline B 2 obtained from feedstock 2 has the most aromatic hydrocarbons and medium RON with regard to other gasolines (RON=92.4). Gasoline B 3 has the most naphthenic and olefinic hydrocarbons and the highest RON (RON=92,8).

Gasoline with a lower sulphur content has lower octane number. Reduction of octane numbers in FCC gasoline occuring in feed hydrotreatment may be regulated through the control of process parameters. It is desirable to conduct the FCC

process in such a way that the reaction temperature is lowered hence encouraging isomerization reactions leading to the generation of iso compounds with high octane number. The octane number in commercial motor gasoline is increased by adding high octane components, such as oxigenates, isomerizates, alkylates and reformates [14, 15].

Gasoline B 1 obtained from hydrodesulphurized feedstock 1 would by its sulphur content be the only one to match the current European specification for motor gasolines, pointing to the need of feeds hydrotreatment.

## 4. CONCLUSIONS

1. The highest conversion was achieved by using hydrotreated feedstock. In the hydrodesulphurization process there occured the increase in the share of paraffinic hydrocarbons from naphthenic hydrocarbons in the feed, considerably upgrading its tendency to crack.

2. Through catalytic cracking, the hydrodesulphurized feed has obtained a higher gasoline yield by 3.5- 6.7 mas. % than the non-hydrodesulphurized feeds, while a decreased LCO yield was recorded in all three feeds.

3. Sulfur content in gasoline created from the hydrodesulphurized feed is lower than that in gasoline obtained from non-hydrotreated feeds. Also, for the same feed, when it comes to sulphur distribution in liquid products, recorded was a higher sulphur share in LCO and HCO, and a lower sulphur content in gasoline.

4. Octane number reduction associated with lowered sulphur content in FCC gasoline is made up for by directing the FCC process towards the production of gasoline with a higher share of iso compounds, while the lack of octane numbers in the motor gasoline pool is made up for by adding isomerizates, alkylates and oxigenates.

5. From the results obtained by the test we may observe that the gasoline obtained from the hydrodesulphurized feedstock 1 is the only one meeting the current specification for motor gasolines by its sulphur content, pointing to the need of hydrotreating the FCC process feed.

**Literatura / References:**

1.  C. Frederich, *Hydrocarbon Processing* **81** (2002)45
2.  E.S. Ellis, J.P. Greeley, E.M. Randtreei, *Petrol. Tehnology Quaterly,* **7** (2002) 59
3.  Specifikacije motormog i dizelskog goriva u Hrvatskoj
4.  P.H. Desai, S.L. Lee, R.J. Jonker, M. de Boer, J. Vrieling, M.S. Sarli, Proceedings Akzo Catalysts Symposium 1994, Hydroprocessing, p 155-174
5.  Gasoline Sulfur Control/IFP North America, Princeton, Hart's Fuel Tehnology @ Managment' s Sulfur, Summer 1998, p 43
6.  L.A. Lacijan, M.W. Schmaith, P.J. Van Opdard, S.G. Simpson, J.G. Woodcock, *Petroleum Tehnology Quaterly,* **7** (2002) 25,
7.  V. Bavaro, World Refinig **10** (2000) 30
8.  P. Magnuson, J. Jakopović, M. Đukić, Inine rafinerije postižu rezulatate smanjenja sumpora u FCC benzinu, Simpozij Goriva 2002.
9.  E.G: Wollaston, W.L. Forsythe, J.A. Vasalos, *Oil and Gas Journal,* **69** (1971) 64
10. R. Sadaghbeigi, FLUID CATALITIC CRACKING, Gulf Publishing Company, Houston, 2002
11.  S. Telen, N. Jambrec, I.B. Beer Romac, *Goriva i maziva,* **42**, 2 (2003) 95
12. J.W. Wilson, FCC TEHNOLOGY AND OPERATION, Pennwell Books, Tulsa 1997
13. G.P.Huling, J. D. Mc Kinneey, T.C. Readal, *Oil and Gas Journal*, **73** (1975) 73
14. S.G.M. van der Lann, *Petroleum Tehnology Quaterly Catalysis,* **8** (2003) 47
15. G.A. Marr, *Petroleum Tehnology Quaterly Catalysis,* **8** (2003) 50

| ključne riječi: | key words: |
|---|---|
| 665.644.26 FCC Fluidni katalitički kreking, frakcije benzina i plinskog ulja | FCC Fluid catalitic cracking, FCC gasoline and gasoil fractions |
| 665.6.033.5 sadržaj sumpora frakcije | fraction sulphur content |
| 665.6.035.3 istraživački oktanski broj IOB frakcije | fraction research octane number RON |
| .002.33 gledište predobrade i izbora sirovina | feedstock pretreatament viewpoint |
| .002.64 gledište rafinacije i finalne dorade produkta | product refining and final treatment viewpoint |

**Autori / Authors:**

mr. sc. Maja Fabulić Ruszkowski, dipl. ing, Sanda Telen, dipl. ing., mr. sc. Štefica Podolski, dipl. ing., mr. sc. Tomislav Šarić, dipl. ing.

INA - Sektor strateškog razvoja, istraživanja i investicija, Lovinčićeva bb, Zagreb