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UTJECAJ POSTUPKA PREDOBRADE FCC SIROVINE NA PRINOSE I SASTAV TEKUĆIH PRODUKATA KREKIRANJA

Sažetak

Sve stroži zahtjevi vezani uz kvalitetu motornih goriva usmjereni su, između ostalog, i na smanjenje količine sumpora u motornim gorivima, što će imati znatan utjecaj i na kvalitetu goriva koja će proizvoditi domaće rafinerije u ovom desetljeću.

Budući da su produkti procesa fluid katalitičkog krekinga glavne komponente motornih goriva, smanjenje sadržaja sumpora u produktima procesa je od prioritetne važnosti, a najefikasnije se provodi procesima hidroobrade sirovine.

U ovom radu je ispitan utjecaj predobrade FCC sirovine na prinose i sastav produkata, s posebnim naglaskom na količinu sumpora u tekućim produktima krekiranja. Predobrada sirovine provedena je na laboratorijskoj aparaturi za ispitivanje procesa hidroobrade, a katalitičko krekiranje provedeno je na MAT-sustavu.

Rezultati provedenih eksperimentalnih ispitivanja pokazuju da hidroobrada FCC sirovine utječe na povećanje prinosa kreking benzina, odnosno smanjenje prinosa cikličkih ulja i koksa, smanjenje sadržaja sumpora u tekućim produktima krekiranja te povećanje udjela izo-parafina u sastavu kreking benzina.

1. UVOD

Zadovoljavanje specifikacija kvalitete motornih goriva koje se u državama Europske Unije (EU) primjenjuju od 2000. godine, kao i onih koji će stupiti na snagu 2005. godine[*], naftne će kompanije prisiliti na ulaganja ogromnih novčanih sredsava. Zadovoljavanje propisanih ograničenja u kvaliteti motornih goriva za 2000. godinu u državama EU provedeno je uspješno uz značajne investicije, pri čemu su najviše problema imale rafinerije temeljene na FCC procesu, a ograničenja koja će stupiti na snagu 2005. godine bit će mnogo teže zadovoljiti. Procjenjuje se da će zbog nemogućnosti udovoljenja tako rigoroznim ograničenjima u kvaliteti goriva u Europi biti prije 2005. zatvoreno 15-20 rafinerija, dok će se preostale rafinerije suočiti s golemim investicijskim ulaganjima.

Računa se da će zbog toga europske naftne kompanije prije 2005. morati uložiti 20-25 milijardi $, u što su uračunate i investicije koje su bile potrebne za zadovoljenje specifikacija koje su stupile na snagu 2000. godine. Više od 65% tog iznosa odnosi se na investicije koje se direktno odnose na dostizanje propisane kvalitete goriva, dok se preostalih 35% odnosi na investicije vezane uz nadogradnju rafinerija, kako bi bile sposobne prerađivati sve teže sirove nafte. Od investicija koje se odnose na postizanje zahtijevane kvalitete goriva oko 70% sredstava bit će utrošeno za dostizanje specifikacija dizelskog goriva, dok će preostalih 30% biti potrebno uložiti za dostizanje specifikacija motornih benzina. Potrebno je naglasiti da ova ogromna ulaganja dolaze u vrijeme kada su rafinerijske marže ionako vrlo niske, što dovodi naftnu industriju u nezavidan položaj.

2. MOGUĆNOSTI SMANJENJA KOLIČINE SUMPORA U PRODUKTIMA FCC PROCESA

Jedan od najvećih izazova s kojim se već suočavaju europske naftne kompanije u nastojanju za smanjenjem zagađenja zraka koje nastaje emisijom štetnih tvari iz benzinskih motora je smanjenje količine sumpora u motornim benzinima, budući da sumpor znatno smanjuje efikasnost automobilskih katalitičkih konvertera. U državama EU od 2000. godine primjenjuje se odredba kojom je ograničena maksimalna količina sumpora u motornim benzinima na 150 mas. ppm, dok će početkom 2005. stupiti na snagu odredba prema kojoj će se količina sumpora u motornim benzinima ograničiti

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[*] Auto Oil Program I i II

na 50 mas. ppm. Budući da sirovine za FCC proces sadrže velike količine sumpora, jasno je da FCC benzin i lako cikličko ulje s FCC procesa predstavljaju glavne izvore sumpora u sastavu motornih benzina, odnosno dizelskog goriva. Procjenjuje se da od FCC benzina, koji u sastavu motornog benzina sudjeluje s udjelom od približno 35 vol.%, potječe i do 98% sumpora, što je ilustrirano primjerom prikazanim u tablici 1.

Tablica 1: Uobičajeni sastav motornog benzina i doprinos pojedinih komponenata ukupnoj količini sumpora u motornom benzinu
Table 1: Typical motor gasoline composition and its components contribution in the total gasoline sulphur quantity

KOMPONENTA MOTORNOG BENZINA	UDIO U MOTORNOM BENZINU (vol. %)	DOPRINOS U KOLIČINI SUMPORA (%)
Alkilat	12	÷
Koking benzin	1	1
Hidrokreking benzin	2	÷
FCC benzin	36	98
Izomerizat	5	÷
Primarni benzin	3	1
Butan	5	÷
MTBE	2	÷
Reformat	34	÷
UKUPNO	100	100

Uz to, na nekim industrijski razvijenim područjima su ograničenja emisije SO_x plinova čak i stroža od ograničenja vezanih uz kvalitetu motornih goriva, a poznato je da se upravo u dimnim plinovima s FCC procesa nalaze ogromne količine tih plinova. Ako tome dodamo da se očekuje i daljnje smanjenje količina sumpora u loživim uljima, kvalitetu teškog cikličkog ulja s FCC procesa potrebno je također uzeti u obzir prilikom odabira strategije za smanjenje sumpora u produktima procesa fluid katalitičkog krekinga.

Izbor strategije za smanjenje količine sumpora u produktima FCC procesa ovisi o konfiguraciji rafinerije, raspoloživosti sirove nafte, sposobnosti rafinerije da prerađuje sirove nafte različitog porijekla i sastava, zahtijevanom udjelu sumpora u produktima, raspoloživom kapitalu te o traženom vremenu povrata investicije. Postoji nekoliko mogućnosti koje stoje na raspolaganju rafinerijama za smanjenje količine sumpora u produktima FCC procesa:

- izbor sirove nafte,
- promjena destilacijskih granica produkata FCC procesa (*undercutting*),

- obradba produkata FCC procesa (*posttreating*),
- predobrada sirovine za FCC proces (*pretreating*).

Slika 1: Raspodjela ukupnog sumpora te olefinske i aromatske frakcije u FCC benzinu
Figure 1: FCC gasoline cumulative sulphur and fractions of olefines and aromatics distribution

2.1. Izbor sirove nafte

Smanjenje količine sumpora u produktima FCC procesa preradom niskosumpornih nafti može se uzeti u obzir ukoliko su cijene sirove nafte na svjetskom tržištu niske i ne postoje značajne razlike u cijeni između slatkih i kiselih sirovih nafti. Ova opcija pogodna je zbog svoje jednostavnosti, jer ne zahtijeva gotovo nikakva investicijska ulaganja. Ipak, ova opcija je neprihvatljiva za rafinerije koje su temeljene na FCC procesu te im FCC benzin predstavlja najznačajniju komponentu motornog benzina. U tom slučaju pomoću te opcije nemoguće je smanjiti količinu sumpora u motornom benzinu na 50 mas. ppm, što propisuju specifikacije za 2005. godinu.

2.2. Promjena destilacijskih granica produkata FCC procesa

Količinu sumpora u FCC benzinu moguće je znatno smanjiti uklanjanjem dijela najteže frakcije FCC benzina. Kao što je vidljivo iz slike 1 koja prikazuje raspodjelu sumpora, olefina i aromata u destilacijskim granicama komponenata FCC benzina, uključivanjem najtežih 20% FCC benzina u frakciju lakog cikličkog ulja može se smanjiti količina sumpora u FCC benzinu za više od 60%. Nedostaci ove opcije očituju se u smanjenom prinosu FCC benzina, povećanom prinosu lakog cikličkog ulja te u tome što ne dolazi do promjena u količini sumpora u ostalim produktima FCC procesa.

2.3. Obrada produkata FCC procesa

Obradba produkata FCC procesa s ciljem zadovoljavanja specifikacija koje ograničavaju količinu sumpora u motornim gorivima zahtijeva znatne investicijske zahvate. Naime, FCC benzin se mora podvrgnuti frakcionaciji, a nakon toga laka i teška frakcija moraju se obrađivati odvojeno. Frakcije se obrađuju odvojeno zato da bi se minimalizirao pad oktanskog broja do kojeg dolazi zbog zasićenja olefina tijekom procesa hidrodesulfurizacije.

Lako cikličko ulje potrebno je obraditi procesima hidroobrade prije namješavanja u dizelsko gorivo, dok je teško cikličko ulje potrebno razrijediti nekom niskosumpornom komponentom. Emisiju SO_x plinova s FCC procesa moguće je smanjiti ugradnjom skrubera.

2.4. Predobrada sirovine za FCC proces

Sve prethodno navedene opcije koje stoje rafinerijama na raspolaganju za smanjenje količine sumpora u motornim gorivima povećavaju rafinerijske troškove, bez ili uz neznatno povećanje dobiti. Stoga se kao najkompletnije rješenje problema prevelikih količina sumpora u motornim gorivima nameće uvođenje vodika u sirovinu za FCC proces, čime se ne rješava samo pitanje prevelike količine sumpora u produktima, već se povećava konverzija i prinosi ekonomski isplativijih produkata FCC procesa. Naime, sumpor i dušik su u teškim frakcijama kemijski vezani u policikličkim aromatskim spojevima koji se vrlo teško cijepaju u FCC procesu. Hidroobradom takve sirovine smanjuje se udio sumpora i dušika te se uvodi vodik u poliaromatske molekule, što dovodi do njihovog lakšeg krekiranja. Na taj način mogu se količine sumpora od 2-3 mas. % u neobrađenoj sirovini reducirati na svega 0.1-0.2 mas. %.

Hidroobrada sirovine poboljšava osobine FCC procesa na nekoliko načina:
- povećava se konverzija u benzin i lakše produkte,
- povećava se prinos FCC benzina,
- smanjuju se prinosi lakog cikličkog i dekantiranog ulja,
- smanjuje se prinos koksa.

Do povećanja prinosa FCC benzina i smanjenja prinosa lakog cikličkog ulja hidroobradom FCC sirovine dolazi zbog povećanja njezine sposobnosti krekiranja u FCC procesu. Ako je hidroobrađena FCC sirovina aromatskog karaktera, ne dolazi do značajnijeg gubitka oktanske vrijednosti FCC benzina, budući da se djelomično zasićeni poliaromatski spojevi iz područja vrelišta dizelskog goriva konvertiraju dajući dodatne količine FCC benzina. Treba imati na umu da se hidroobradom neće poboljšati cetanska vrijednost lakog cikličkog ulja, jer u njegovom sastavu ipak zaostaje visoki udio aromata.

Dakle, hidroobradom FCC sirovine dolazi do povećanja prinosa motornih goriva, a time i poboljšanja ekonomičnosti rafinerije, što je osobito izraženo kod "benzinskih rafinerija". Ipak, kemizam kojim nastaju ugljikovodici iz destilacijskih granica kreking benzina, dovodi i do nastajanja lakog cikličkog ulja te dekantiranog ulja s visokim udjelima aromatskih ugljikovodika. Zbog toga količina lakog cikličkog ulja koja se može namiješati u dizelsko gorivo nije ograničena samo sadržajem sumpora, već i niskom cetanskom vrijednošću. Budući da će se u državama EU od 2005. godine primjenjivati specifikacije koje ograničavaju količinu sumpora u dizelskom gorivu na 50 mas. ppm, a pretpostavlja se da će propisana vrijednost cetanskog broja dizelskog goriva biti 56, jasno je da će se kvaliteta lakog cikličkog ulja s FCC procesa morati podići na višu razinu. Bolju kvalitetu lakog cikličkog ulja neće biti moguće realizirati samo hidrodesulfurizacijom sirovine za FCC proces, već će postrojenje za predobradu FCC sirovine morati biti i djelomično konverzijsko postrojenje.

3. EKSPERIMENTALNI DIO

U eksperimentalnim istraživanjima korištena je sirovina za FCC proces koja se sastojala od približno 30 vol.% atmosferskog teškog plinskog ulja, dok su ostatak do 100% bila vakuum plinska ulja (sirovina 1). Sirovina je laboratorijski hidrodesulfurizirana na aparaturi za hidroobradu (sirovina 2), a dio hidrodesulfurizirane sirovine je na istoj aparaturi podvrgnut blagom hidrokrekingu (sirovina 3). Jedan dio početne neobrađene sirovine podvrgnut je direktno blagom hidrokrekingu bez prethodne hidrodesulfurizacije (sirovina 4). Tako dobivene četiri sirovine, čija su fizikalno-kemijska svojstva prikazana u tablici 2, podvrgnute su zatim katalitičkom krekingu na laboratorijskom uređaju, tzv. MAT-sustavu (*eng. microactivity test*).

Eksperimentalni uvjeti primijenjeni u procesima hidrodesulfurizacije i blagog hidrokrekinga prikazani su u tablici 3, dok su eksperimentalni uvjeti primijenjeni prilikom katalitičkog krekinga na MAT-sustavu prikazani u tablici 4.

Tablica 2: Fizikalno-kemijska svojstva upotrijebljenih sirovina
Table 2: Physical and chemical properties of used feedstocks

SVOJSTVO	SIROVINA 1	SIROVINA 2	SIROVINA 3	SIROVINA 4
Gustoća na 15 ^{0}C, g/cm^3	0.8818	0.8671	0.8592	0.8691
Stupnjevi API	29.0	31.6	33.1	31.3
Viskoznost (40 ^{0}C), mm^2/s	14.53	12.18	12.12	13.41
Viskoznost (100 ^{0}C), mm^2/s	3.29	2.91	3.05	3.15
Tecište, ^{0}C	+30	+27	+30	+30
Indeks loma n_D^{20}	1.4938	1.4818	1.4764	1.4840
Količina sumpora, mas. %	0.990	0.064	0.015	0.089
Srednja molekulska masa	330	340	345	350
n-d-M analiza: % C_A	15.45	17.06	14.52	18.27
% C_N	22.02	10.21	5.84	3.71
% C_P	62.53	72.73	79.64	78.01
R_A	0.59	0.71	0.61	0.79
R_N	0.98	0.50	0.27	0.16
R_T	1.57	1.21	0.88	0.95

Tablica 3: Eksperimentalni uvjeti primijenjeni u procesima hidrodesulfurizacije i blagog hidrokrekinga polazne sirovine
Table 3: Experimental conditions applied in initial feedstock hydrodesulfurization and mild hydrocracking processes

PARAMETAR	DESULFURIZACIJA	BLAGI HIDROKREKING
Temperatura u reaktoru, ^{0}C	360	330
Tlak u reaktoru, bar	65	65
Omjer vodika i sirovine	170	300
Prostorna brzina (LHSV), h^{-1}	1.00	0.50

Tablica 4: Eksperimentalni uvjeti primijenjeni prilikom katalitičkog krekinga na MAT-sustavu
Table 4: Experimental conditions applied in the MAT-system catalytic cracking

PARAMETAR	VRIJEDNOST
Omjer katalizatora i sirovine (C/O omjer)	3.01
Prostorna brzina (WHSV), h^{-1}	15.96
Temperatura reaktora, ^{0}C	510-540
Temperatura regeneracije katalizatora, ^{0}C	650
Vrijeme kontakta sirovine i katalizatora, s	75
Vrijeme trajanja regeneracije, s	2400

U sva tri slučaja primijenjeni su komercijalni katalizatori za rafinerijske procese hidrodesulfurizacije, blagog hidrokrekinga, odnosno katalitičkog krekinga u fluidiziranom sloju. Prinosi pojedinih komponenata tekućeg produkta krekiranja izračunati su na osnovi eksperimentalnih podataka dobivenih kromatografskom metodom simulirane destilacije. Strukturni sastav tekućeg produkta krekiranja (PIONA analiza) određivan je na plinskom kromatografu s predfrakcionatorom, dok je sadržaj sumpora u tekućem produktu krekiranja određivan mikrokulometrijski.

4. REZULTATI I RASPRAVA

Obradbom u procesima hidrodesulfurizacije i blagog hidrokrekinga znatno je povećana kvaliteta sirovine za FCC proces, što je vidljivo iz tablice 2, koja prikazuje fizikalno-kemijska svojstva neobrađene sirovine i triju hidroobrađenih sirovina. Iz rezultata n-d-M analize vidljivo je da se udio naftenskog ugljika hidrodesulfurizacijom FCC sirovine na poluindustrijskom postrojenju smanjio s početnih 22% na 10%, a blagim hidrokrekingom hidrodesulfurizirane sirovine smanjio se za dodatnih 4%. Također dolazi i do smanjenja udjela aromatskog ugljika. Uzrok tih pojava je cijepanje peteročlanih i šesteročlanih prstenova s heteroatomom (sumpor, dušik, kisik), pri čemu dolazi do stvaranja olefinskih, parafinskih i aromatskih ugljikovodika s manjim brojem prstenova.

Tablica 5: Utjecaj postupka predobrade sirovine i temperature reaktora na konverziju i raspodjelu produkata katalitičkog krekinga na MAT-sustavu

Table 5: Influence of feedstock pretreatment method and reactor temperature on conversion and cracking products distribution in MAT-system

TEMPERATURA REAKTORA, ^{0}C	OZNAKA SIROVINE	KONVERZIJA mas. %	PRINOS BENZINA, mas.%	PRINOS LCU mas. %	PRINOS TCU mas. %	PRINOS KOKSA mas %
510	SIROVINA 1	68.28	45.03	21.88	9.84	3.54
	SIROVINA 2	74.99	51.55	18.35	6.66	2.92
	SIROVINA 3	81.81	55.39	14.51	3.68	2.68
	SIROVINA 4	70.75	48.71	21.61	7.64	3.14
520	SIROVINA 1	71.42	45.27	19.51	9.06	4.10
	SIROVINA 2	76.88	50.36	18.43	4.69	3.64
	SIROVINA 3	81.26	55.26	14.09	4.65	3.31
	SIROVINA 4	73.94	49.58	19.17	6.89	3.46
530	SIROVINA 1	71.74	44.79	18.32	9.93	3.97
	SIROVINA 2	77.66	49.28	17.86	4.48	3.44
	SIROVINA 3	81.53	55.08	15.09	3.38	3.29
	SIROVINA 4	76.44	51.32	17.28	6.28	3.53
540	SIROVINA 1	71.70	42.89	18.53	9.77	4.45
	SIROVINA 2	78.62	49.49	16.76	4.62	3.47
	SIROVINA 3	83.69	55.68	13.21	3.10	3.39
	SIROVINA 4	76.59	50.07	16.92	6.49	3.02

Nastali olefinski ugljikovodici odmah se zasićuju vodikom tvoreći parafine. To je razlog zbog kojeg je udio parafinskog ugljika s vrijednosti od 62% u neobrađenoj FCC sirovini porastao na gotovo 80% nakon hidrodesulfurizacije i blagog hidrokrekiranja iste sirovine.

Hidrodesulfurizacijom neobrađene FCC sirovine postignuto je 93%-tno uklanjanje sumpora, dok je blagim hidrokrekingom hidrodesulfurizirane sirovine uklonjeno dodatnih 5% sumpora, dakle ukupno 98% u odnosu na neobrađenu FCC sirovinu. Postupkom blagog hirokrekinga FCC sirovine bez prethodne hidrodesulfurizacije ostvareno je 91%-tno uklanjanje sumpora.

Slika 2: Utjecaj postupka predobrade sirovine i temperature reaktora na MAT konverziju
Figure 2: Influence of feedstock pretreatment method and reactor temperature on MAT conversion

Utjecaj postupaka hidroobrade na ostvarene konverzije i raspodjelu produkata krekiranja na MAT-sustavu vidljiv je iz tablice 5. Poznato je da se procesom katalitičkog krekiranja najlakše cijepaju parafinske sirovine, što se očituje povećanjem konverzije. Iz slike 2 vidljivo je da su hidrodesulfurizirana sirovina 2 i blago hidrokrekirana sirovina 3 najreaktivnije u procesu katalitičkog krekiranja, što je osobito izraženo pri višim temperaturama reaktora. Uzrok tome je upravo povećanje udjela parafinskih ugljikovodika u procesima hidrodesulfurizacije i blagog hidrokrekinga, kao što je već rečeno.

Slika 3: Utjecaj postupka predobrade sirovine i temperature reaktora na prinos kreking benzina
Figure 3: Influence of feedstock pretreatment method and reactor temperature on FCC gasoline yield

Slika 4: Utjecaj postupka predobrade sirovine i temperature reaktora na prinos lakog cikličkog ulja
Figure 4: Influence of feedstock pretreatment method and reactor temperature on light cycle oil yield

Također je opaženo da se procesom blagog hidrokrekinga neobrađene sirovine dobiva FCC sirovina koja sadrži gotovo isti udio parafinskog ugljika kao i hidrodesulfurizirana i blago hidrokrekirana sirovina, ali se prilikom njezinog krekiranja na nižim temperaturama reaktora ostvaruju tek nešto veće konverzije u odnosu na neobrađenu sirovinu. Ovu pojavu moguće je objasniti prisustvom parafina koji se nalaze u bočnim lancima alkilaromata, a za čije su krekiranje potrebne više temperature reaktora.

Ostvareni prinosi kreking benzina i lakog cikličkog ulja (LCU) katalitičkim krekiranjem na MAT-sustavu u ovisnosti o upotrijebljenoj sirovini i temperaturi reaktora prikazani su na slikama 3 i 4.

Tablica 6: Utjecaj postupka predobrade sirovine za katalitički kreking i temperature reaktora na sastav kreking benzina i količinu sumpora u tekućem produktu krekiranja na MAT-sustavu

Table 6: Influence of FCC feedstock pretreatment method and reactor temperature on FCC gasoline composition and sulphur quantity in the MAT-system liquid cracking product

TEMPERAT. REAKTORA ^{0}C	OZNAKA SIROVINE	UDIO izo-PARAFINA mas. %	UDIO n-PARAFINA mas. %	UDIO OLEFINA mas. %	UDIO NAFTENA mas. %	UDIO AROMATA mas. %	KOLIČINA SUMPORA mas. %
510	SIR. 1	37.42	5.92	5.15	15.14	36.31	0.710
	SIR. 2	42.96	4.82	3.89	17.26	31.04	0.064
	SIR. 3	44.41	3.71	3.73	18.38	29.62	0.011
	SIR. 4	42.24	5.38	3.45	17.73	31.10	0.070
520	SIR. 1	34.31	6.08	5.83	16.22	37.51	0.680
	SIR. 2	41.45	4.91	4.46	16.33	32.82	0.059
	SIR. 3	42.47	3.78	3.31	18.82	31.52	0.009
	SIR. 4	40.08	5.40	3.94	16.71	33.76	0.066
530	SIR. 1	32.76	6.47	6.25	16.36	38.14	0.600
	SIR. 2	39.97	5.26	4.31	15.76	34.66	0.045
	SIR. 3	41.63	4.87	2.38	17.48	33.56	0.008
	SIR. 4	37.51	5.66	4.56	16.16	36.02	0.062
540	SIR. 1	29.77	6.91	8.96	13.98	40.33	0.510
	SIR. 2	33.36	5.64	7.48	16.34	37.15	0.043
	SIR. 3	41.08	5.22	3.43	16.51	33.69	0.008
	SIR. 4	36.22	5.82	5.18	15.29	37.31	0.061

Prinosi FCC benzina pokazuju slične promjene kao i konverzije u procesu. Vidljivo je da se hidrodesulfurizacijom i blagim hidrokrekiranjem FCC sirovine ostvaruju veći prinosi kreking benzina za oko 10 mas.% u odnosu na neobrađenu sirovinu. Istodobno, prinosi lakog cikličkog ulja smanjuju se ovisno o temperaturi reaktora za 3.5-6 mas.%, teškog cikličkog ulja za 4.5-6.5

mas.%, a prinosi koksa padaju za 0.7-0.8 mas.%. Sirovina dobivena blagim hidrokrekingom, bez prethodne hidrodesulfurizacije, daje lošiju raspodjelu produkata u usporedbi prema hidrodesulfuriziranoj sirovini. Uzrok tome je veći udio zaostalih aromatskih policikličkih struktura u toj sirovini, čime je uvjetovano nastajanje viših prinosa težih produkata uz veće udjele sumpornih i dušičnih spojeva.

Slika 5: Utjecaj postupka predobrade sirovine i temperature reaktora na udio izo-parafinskih ugljikovodika u sastavu kreking benzina
Figure 5: Influence of feedstock pretreatment method and reactor temperature on the share of iso-paraffinic hydrocarbons in FCC gasoline composition

Utjecaj postupka hidroobrade sirovine za katalitički kreking i temperature reaktora na sastav kreking benzina i količinu sumpora u tekućem produktu krekiranja na MAT-sustavu vidljiv je iz tablice 6. U procesu katalitičkog krekinga odvijaju se reakcije prijelaza vodika, koje su egzotermne, što znači da povišena temperatura reaktora uvjetuje slabljenje njihovog utjecaja. Na taj način dolazi do smanjenja udjela ukupnih parafinskih, kao i povećanja udjela olefinskih ugljikovodika u sastavu kreking benzina, što je vidljivo na slikama 5, 6 i 7.

U samoj strukturi parafinske frakcije kreking benzina vidljivo je da povećanjem temperature reaktora dolazi do izrazitog smanjenja prinosa izo-parafina, dok se prinos n-parafina neznatno povećava, tako da se ukupni prinos parafinskih ugljikovodika smanjuje. Do smanjenja prinosa izo-parafinskih ugljikovodika s povećanjem temperature reaktora dolazi zbog slabljenja utjecaja egzotermnih reakcija izomerizacije.

Slika 6: Utjecaj postupka predobrade sirovine i temperature reaktora na udio n-parafinskih ugljikovodika u sastavu kreking benzina
Figure 6: Influence of feedstock pretreatment method and reactor temperature on the share of n-paraffinic hydrocarbons in FCC gasoline composition

Ako promatramo ovisnost udjela parafinskih i olefinskih ugljikovodika u sastavu kreking benzina o oštrini predobrade sirovine za proces katalitičkog krekinga, vidljivo je da se s povećanjem oštrine predobrade sirovine povećava udio parafinskih, a smanjuje udio olefinskih ugljikovodika u sastavu kreking benzina, kao posljedica hidroobrade sirovine.

U ovom slučaju može se također uočiti da udjeli n-parafina i izo-parafina u benzinu ovise o oštrini hidroobrade sirovine za katalitički kreking. Tako s povećanjem oštrine hidroobrade raste udio izo-parafina, a smanjuje se udio n-parafina. Budući da n-parafini izrazito smanjuju oktansku vrijednost, a izo-parafini su poželjne oktanske komponente, vidljiv je pozitivan utjecaj povećanja oštrine hidroobrade na svojstva kreking benzina, osobito ako se u procesu katalitičkog krekinga primjenjuju niže temperature reaktora.

Udio naftenskih ugljikovodika u sastavu kreking benzina smanjuje se s porastom temperature reaktora, a raste s povećanjem oštrine predobrade sirovine za proces katalitičkog krekinga, što je vidljivo iz slike 8. Naftenski ugljikovodici mogu u procesu katalitičkog krekinga nastati ciklizacijom olefina.

Slika 7: Utjecaj postupka predobrade sirovine i temperature reaktora na udio olefinskih ugljikovodika u sastavu kreking benzina
Figure 7: Influence of feedstock pretreatment method and reactor temperature on the share of olefinic hydrocarbons in FCC gasoline composition

Slika 8: Utjecaj postupka predobrade sirovine i temperature reaktora na udio naftenskih ugljikovodika u sastavu kreking benzina
Figure 8: Influence of feedstock pretreatment method and reactor temperature on the share of naphthenic hydrocarbons in FCC gasoline composition

Budući da se krekiranjem hidrodesulfurizirane i blago hidrokrekirane sirovine dobiva najveći udio naftena u sastavu kreking benzina, a iz njezinih fizikalno-kemijskih svojstava vidljiv je nizak udio naftenskog ugljika, može se zaključiti da je najveći dio naftena u sastavu kreking benzina nastao ciklizacijom olefina. Kako udio olefinskih ugljikovodika u motornom benzinu predstavlja jedan od ograničenih parametara njegovog sastava (u državama EU od 2000. godine dopušteno je max. 18 vol. %, a za 2005. godinu ograničenje još nije postavljeno), u procesu katalitičkog krekinga trebalo bi primjenjivati niže temperature reaktora, želi li se smanjiti udio olefina u sastavu kreking benzina.

Aromatski ugljikovodici koji se nalaze u sastavu kreking benzina mogu nastati krekiranjem bočnih lanaca aromatskih ugljikovodika iz sirovine, pri čemu nastaju nesupstituirani aromati ili transalkilacijom aromata iz sirovine, pri čemu nastaju aromati s drukčijim alkilnim lancima od početnog aromata. Aromatski ugljikovodici mogu nastati i reakcijama dehidrogenacije naftena.

Slika 9: Utjecaj postupka predobrade sirovine i temperature reaktora na udio aromatskih ugljikovodika u sastavu kreking benzina
Figure 9: Influence of feedstock pretreatment method and reactor temperature on the share of aromatic hydrocarbons in FCC gasoline composition

Iz slike 9 vidljivo je da povećanjem temperature reaktora raste udio aromatskih ugljikovodika u sastavu kreking benzina zbog toga što su reakcije krekiranja i dehidrogenacije endotermne reakcije, te im pogoduju više temperature reaktora. Istodobno, udio aromatskih ugljikovodika u sastavu kreking benzina smanjuje se s povećanjem oštrine predobrade sirovine za katalitički kreking. Razlog tome je u činjenici da se hidrodesulfurizacijom i blagim hidrokrekingom sirovine provodi hidrogenacija aromatskih ugljikovodika koji u sebi sadrže atome sumpora, dušika i kisika, pri čemu nastaju odgovarajući parafinski ugljikovodici uz sumporovodik, amonijak i vodu. Zbog toga je udio aromata u predobrađenoj sirovini znatno manji u usporedbi s neobrađenom sirovinom, što ima utjecaj na udio aromata u sastavu kreking benzina. Budući da su aromatski ugljikovodici najznačajnije oktanske komponente kreking benzina, jasno je da povećanje oštrine hidroobrade sirovine za katalitički kreking negativno utječe na oktanski broj dobivenog kreking benzina.

Slika 10: Utjecaj postupka predobrade sirovine i temperature reaktora na količinu sumpora u tekućem produktu krekiranja na MAT-sustavu
Figure 10: Influence of feedstock pretreatment method and reactor temperature on sulphur quantity in the MAT-system liquid cracking product

Zbog ograničenosti postojeće analitičke opreme, količinu sumpora nije bilo moguće odrediti u kreking benzinu, već je ona određivana u ukupnom tekućem produktu katalitičkog krekiranja na MAT-sustavu. Kao što je vidljivo iz rezultata na slici 10, količina sumpora u tekućem produktu katalitičkog krekinga lagano se smanjuje s porastom temperature reaktora, radi povećane vjerojatnosti cijepanja ravnolančanih i cikličkih spojeva koji sadrže atom sumpora, pri čemu nastaje odgovarajući parafin i sumporovodik.

Iz slike 10 vidljivo je također naglašeno smanjenje količine sumpora u tekućem produktu krekiranja s povećanjem oštrine hidroobrade sirovine za proces katalitičkog krekinga. Tako tekući produkt katalitičkog krekinga dobiven krekiranjem hidrodesulfurizirane sirovine, ovisno o temperaturi reaktora, sadrži 430-640 mas. ppm sumpora, dok tekući produkt dobiven krekiranjem hidrodesulfurizirane i blago hidrokrekirane sirovine sadrži 80-110 mas. ppm sumpora. Istodobno, tekući produkt dobiven katalitičkim krekiranjem blago hidrokrekirane sirovine bez prethodne hidrodesulfurizacije sadrži 610-700 mas. ppm sumpora. Ako se želi zadržati količina kreking benzina koja se namješava u sastav motornih benzina (oko 35 vol. %), dokazano je da radi zadovoljenja specifikacija koje u državama EU stupaju na snagu 2005. godine, kreking benzin može sadržavati maksimalno 135 mas. ppm sumpora. Taj kriterij u našem slučaju zadovoljava sigurno benzin dobiven katalitičkim krekiranjem hidrodesulfurizirane i blago hidrokrekirane sirovine, a najvjerojatnije i benzin dobiven krekiranjem samo hidrodesulfurizirane sirovine pri višim temperaturama reaktora. Istodobno, kreking benzin dobiven krekiranjem sirovine koja je prethodno bila podvrgnuta samo blagom hidrokrekingu ne zadovoljava spomenute specifikacije.

5. ZAKLJUČAK

Iz iznesenih literaturnih podataka i dobivenih eksperimentalnih rezultata mogu se izvesti sljedeći zaključci na temu utjecaja postupka predobrade sirovine za proces katalitičkog krekinga na prinose i količinu sumpora u produktima katalitičkog krekiranja:

- Hidroobradom sirovine procesa katalitičkog krekinga dolazi do povećanja udjela parafinskih ugljikovodika pretvorbom pretežito naftenskih, a u manjem obimu aromatskih ugljikovodika, čime se znatno povećava njezina sklonost krekiranju, koja se očituje u povećanju konverzije.
- Katalitičkim krekiranjem hidrodesulfurizirane sirovine, koje je provedeno na MAT-sustavu, ostvareno je povećanje prinosa benzina 5-6 mas. %, dok je katalitičkim krekiranjem hidrodesulfurizirane i blago hidrokrekirane sirovine ostvareno oko 10 mas. % više kreking benzina u usporedbi prema krekiranju neobrađene sirovine.
- Istovremeno s povećanjem prinosa kreking benzina dolazi do smanjenja prinosa lakog i teškog cikličkog ulja, kao i koksa.

- Povećanjem oštrine predobrade sirovine za katalitički kreking, u kreking benzinu povećava se udio izo-parafinskih i naftenskih, a smanjuje udio olefinskih i aromatskih ugljikovodika. U procesu katalitičkog krekinga treba primijeniti procesne uvjete koji omogućuju da se smanjenje oktanskog broja nastalo zbog smanjenja udjela aromatskih ugljikovodika u kreking benzinu kompenzira povećanjem udjela izo-parafina.
- Nadolazeće specifikacije vezane uz količinu sumpora u motornim benzinima, koje će se u državama EU primjenjivati od 2005. godine, sigurno se mogu zadovoljiti namješavanjem nepromijenjenih količina benzina dobivenog krekiranjem hidrodesulfurizirane i blago hidrokrekirane sirovine, a vrlo vjerojatno i namješavanjem benzina dobivenog krekiranjem samo hidrodesulfurizirane sirovine pri višim temperaturama reaktora. Istodobno, namješavanjem kreking benzina dobivenog krekiranjem sirovine koja je predobrađena samo postupkom blagog hidrokrekinga to neće biti ostvarivo.
- Ako rezimiramo sve navedene činjenice, vidljivo je da predobrada sirovine za proces katalitičkog krekinga nije opcija koja predstavlja samo trošak za rafinerije, koji je nužan za proizvodnju motornih goriva u skladu s nadolazećim specifikacijama, već se predobradom postiže bolja valorizacija sirovine za proces katalitičkog krekinga. Time se znatno povećava ekonomičnost rafinerija temeljenih na procesu katalitičkog krekiranja u fluidiziranom sloju.

INFLUENCE OF FCC FEEDSTOCK PRETREATMENT PROCESS ON COMPOSITION AND YIELDS OF LIQUID CRACKING PRODUCTS

Abstract

Ever more rigorous requirements for the quality of motor fuels are directed additionally towards the reduction of gasoline sulphur content. It is certain that this trends will also have a significant impact on the quality of fuels to be produced by domestic refineries throughout this decade.

Since the products obtained via fluid catalytic cracking are the main components of motor fuels, the removal of sulphur from process products is of extreme priority, and it is provided by feedstock hydrocracking as the most effective method.

The aim of this study is to analyse the influence of FCC feedstock pretreatment on yields and composition of products, as well as the sulphur quantity in liquid cracking products. Feedstock pretreatment was performed in laboratory hydrotreatment process testing equipment, and catalytic cracking on the MAT-system.

The results of experimental testing show that hydrotreatment of FCC feedstock has an influence on increasing of cracking gasoline and lowering the yield of cyclic oil and coke, sulphur content in liquid cracking products and increase of isoparaffin in cracking gasoline compounds.

1. INTRODUCTION

The oil companies will be forced to invest substantial funds to meet the law regulations referring to gasoline quality standards, applied since 2000 by the EU, and those to be enforced in 2005 (Auto Oil Program I and II).

While the fulfilment of the prescribed motor fuel quality standars by the EU in 2000, was successfully carried out under the considerable investments, the biggest problems appeared nevertheless with the refineries based on FCC process. The standards to be set in motion in 2005, are not going to be met so easily. As a result of the inability to satisfy the rigorous motor fuel quality limitations, the closing of about 15-20 refineries in Europe is expected before 2005, while the rest is going to face capital investments. The evaluations are made showing that European oil companies will have to invest 20-25 billions of $ before 2005, with funds required for covering the specifications enforced in 2000 incalculated. More than 65% of above sum directly refers to the investments into given fuel standards, and the remaining 35% to the investments into the construction of refinery annexes, for their adaptation to the processing of still more heavier crude oil.

With reference to the investments into the required fuel quality upgrading, about 70% of the funds will be spent on reaching diesel fuel specifications, while the rest of 30% is going to be required for motor gasoline specifications. It should be emphasized that these enormous investments will come at the moment of refineries network being on a very low level already, what will bring the oil industry into an enviable position.

2. POSSIBILITIES OF SULPHUR REDUCTION IN FCC PRODUCTS

One of the greatest challenges the European oil companies have already experienced in their attempt of reducing air pollution caused by the gasoline driven motors harmful particles emmission, is the reduction of fuels sulphur, as sulphur significantly reduces the efficiency of automobile catalytic converters. As shown in the Table 1, the EU has been applying since 2000, the regulation by which the highest motor gasoline sulphur quantity has been reduced to 150 mas. ppm, while at the beginning of the year 2005, the provision will be brought according to which the motor gasoline sulphur quantity will be reduced to 50 mas. ppm. Due to a high FCC feedstock sulphur content, it is obvious that FCC gasoline and a light cyclic FCC oil, represent the main sulphur sources in the motor gasoline composition, or diesel fuel. It has been estimated, that from FCC gasoline, contributing with the ratio of approximately 35 vol.% in the motor gasoline composition, originates even up to 98% of sulphur, as illustrated by the sample in the Table 1. Besides, in some industrially developed areas the emmissions of SO_x gases are more restricted than the limitations related to the quality of motor fuels, and it has been known that in stack gases from FCC process there are enormous quantities of such gases present. If we add to this that further reduction of fuel oil sulphur is expected, the quality of heavy cyclic FCC oils should also be taken into consideration when deciding upon the strategy of fluid catalytic cracking process products sulphur reduction.

Determination of FCC products sulphur reduction strategy depends upon the refinery configuration, crude oil resources, capacities of crude oil processing from various origins and compositions, required products sulphur contribution, available funds and the required term of investment repayment. There are several options for refineries related to FCC products sulphur reduction:

- crude selection,
- FCC products distilation limits undercutting,
- FCC products posttreating,
- FCC feedstock pretreating

2.1. Crude selection

FCC products sulphur reduction by processing of low grade sulphur crude oils could be considered in terms of the world’s low crude oil market price, and insignificant difference between sweet and sour crude price. This option is favourable, owing to its simplicity, and as requiring almost no investments. However, it is unaceptable for refineries based on FCC, since FCC gasoline is representing the most important component of motor gasoline. Here it is impossible to reduce the motor gasoline sulphur quantity to 50 mas. ppm. as required for 2005 specifications.

2.2. FCC products distillation limit undercutting

A significant FCC gasoline cumulative sulphur reduction is made possible by the removal of the part of the heaviest FCC gasoline fraction. As shown in the Figure 1 illustrating cumulative sulphur, olefines fractions and aromatics distribution within FCC gasoline components distillation limits, including the heaviest 20% of FCC gasoline distribution in light cyclic oil fraction, FCC gasoline cumulative sulphur could be reduced for over 60%. The disadvantage of the option reflects in the reduced FCC gasoline contribution, increased light cyclic oil contribution, and no change of sulphur quantity in other FCC products.

2.3. FCC products posttreating

FCC product treatment with the scope of meeting the specifications restricting motor fuel sulphur quantity require substatial investments. Namely, FCC gasoline should be subjected to fractioning, and light and heavy fractions treated separately thereupon. The fractions must be separately treated as to minimize the possibility of octane number reduction, caused by olefine saturation in the process of hydrodesulphurization. Light cycle oil should be diluted by a low sulphur component. The emission of SO_x gases from FCC processes could be reduced by scrubber installation.

2.4. FCC feedstock pretreating

All previously mentioned options left to refineries for motor fuel sulphur reduction increase the refinery’s expences, with no or a very small profit increase. Therefore, the idea of hydrogen introduction into FCC feedstock, as the most complete solution for elimination of the problem of extremely high sulphur quantities in motor fuel, has come up, and it will solve not only the very question of the overdosed product sulphur, but shall also increase the conversion and the economic yield of cost-effective FCC products. Namely, sulphur and nitrogen in heavy fractions are chemicaly binded in polycyclic compounds, and could be hardly cracked in FCC process. Hydrocracking of such feedstock reduces the ratio of sulphur and nitrogen, and introducing hydrogen into polyaromatic molecules, brings to their easier cracking. In such a way, the sulphur quantities of 2-3 mas.% in non-treated feedstock could be reduced just to 0.1-0.2 mas.%. Feedstock hydrocracking improves the properties of FCC process in several directions:

- increased conversion into gasoline and ligher products
- increased yields of FCC gasoline
- reduced yields of light cycle and decanted oil
- reduced coke yield

The increased FCC gasoline yields and reduction of light cycle oil yield by FCC feedstock hydrocracking is rendered by its increased crackability in FCC process. If hydrocracked FCC feedstock is of aromatic nature, there is no significant loss of FCC gasoline octane value, since the partially saturated polyaromatic compounds in diesel fuel boiling point are converted, producing additional FCC gasoline quantities. It must be kept in mind that hydrocracking shall not improve the cetane value of light cycle oil, as its composition is lacking a high level of aromatics nontheless.

Consequently, hydrocracking of FCC feedstock renders increased yields of motor fuels, improving thus refinery cost-efficiency, what is specially accentuated by gasoline refineries. However, a chemistry forming hydrocarbons from distillation cracking gasoline margines, also brings to the formation of light cycle and decanted oil, with high portions of aromatic hydrocarbons. That is why the quantity of light cycle oil able to be mixed into diesel fuel, has not been restrained only by the sulphur content, but also by the low cetane value.

As the EU is going to apply the specifications limiting diesel fuel sulphur quantity to 50 mas. ppm from 2005 on, it has been expected that the prescribed value of diesel cetane number will be 56, and surely the quality of light cycle oil from FCC process will have to be brought to a higher level. The improved quality of light cycle oil will not be achieved solely by hydrodesulphurization of FCC feedstock, but also by applying FCC feedstock pretreatment equipment that will have to be partially a converter.

3. EXPERIMENTAL

In experimental studies a standard FCC feedstock was used, composed of approximately 30 vol.% of heavy atmospheric gas oil, and the remaining part to 100% of vacuum gas oils (feedstock 1). The feedstock was hydrodesulphurized in hydrocracking apparatus (feedstock 2), and a part of hydrodesulphurized feedstock was subjected to mild hydrocracking in the same apparatus (feedstock 3). A part of initial non-treated feedstock was subjected to direct mild hydrocracking without being previously hydrodesulphurized (feedstock 4). Four feedstocks obtained in such a way, with physical and chemical properties shown in the Table 2, were further subjected to a catalytic cracking in laboratory microactivity test equipment, named MAT-system. Experimental conditions applied in the processes of hydrodesulphurization and mild hydrocracking are shown in the Table 3, and the experimental conditions applied in catalytic cracking in MAT-system, are shown in the Table 4.

In all the three mentioned cases, the commercial catalyst was used in hydrodesulphurization refining processes, and mild hydrocracking, or fluid catalytic cracking. The yields of certain fluid product cracking components were assessed on the basis of the experimental data achieved from chromatographic method of simulated distillation. Structural composition of fluid cracking product (PIONA analysis) was determined by a gas chromatograph with prefractionator, and fluid cracking product sulphur quantity was microcoulometrically determined.

4. RESULTS AND DISCUSSION

Hydrodesulphurization treatments and mild hydrocracking have significantly increased the quality of FCC feedstock, as illustrated in Table 2 together with physical and chemical properties of non-treated feedstock and three hydrocracked feedstocks. The results of n-d-M analysis show that the share of crude oil carbon by hydrodesulphurization of FCC feedstock on semi-industrial equipment, was reduced from the initial 22% to 10%, and by a mild feedstock hydrocracking for additional 4%. The share of aromatic carbon is also reduced as shown by analyzing. Such phenomena are caused by cracking of five-member and six-member rings with heteroatom (sulphur, nitrogen, oxygen), when olefinic, paraffinic and aromatic hydrocarbons are formed with lower number of rings. The developed olefine hydrocarbons are instantly saturated with hydrogen forming paraffines. This is the reason why the share of paraffinic carbon has increased from 62% in non-treated feedstock to almost 80% after hydrodesulphurization and mild hydrocracking of the same feedstock.

By hydrodesulphurization of non-treated FCC feedstock a 93% sulphur elimination has been achieved, and mild hydrocracking of desulphurized feedstock brought to the elimination of further 5% of sulphur, and the overall of 98%, in relation to the non-treated FCC feedstock. By mild hydrocracking of non predesulphurized FCC feedstock, a 91% elimination of sulphur has been achieved.

The influence of hydrocracking on effected conversions and distribution of cracking products on MAT-system is shown in Table 5. The process of catalytic cracking is known as the easiest way of paraffinic feedstock cracking, as reflected in increased conversion. Figure 2 shows that hydrodesulphurized feedstock 2 and mildly hydrocracked feedstock 3 are most reactive in catalytic cracking process, what is particularly manifested at higher reactor temperatures. The increased share of paraffinic hydrocarbons is a direct issue of hydrodesulphurization processes and mild hydrocracking, as previously discussed. In the process of non-treated feedstock mild cracking, obtaining of FCC feedstock with almost equal paraffinic carbon share as hydrodesulphurized and mildly cracked feedstock is notable, though by its cracking at lower reactor temperatures slightly higher conversions are obtained, compared to non-treated feedstock. This can be explained by the presence of paraffines, present in side chains of alkylaromates for whose cracking higher reactor temperatures are required.

Yields of cracking gasoline and a light cycle oil (LCO) in catalytic cracking in MAT-system depend on used feedstock and reactor temperature shown in figures 3 and 4. The yields of FCC gasoline indicate similar changes as conversions in process. It is noted that hydrodesulphurization and FCC feedstock mild hydrocracking renderabout 10 mas.% higher cracking gasoline yields, in relation to non-treated feedstock. Simultaneously the yields of light cycle oil are reduced for 3,5-6 mas.%, as depending on the reactor temperature, and the yields of heavy cycle oil for 4.5-6.5 mas.%, and coke yields for 0.7-0.8 mas.%. Feedstock produced by mild hydrocracking of non-predesulphurized FCC feedstock, renders worse distribution of products in comparison with hydrodesulphurized feedstock. It is caused by the higher share of residual aromatic polycyclic structures that bring to the formation of higher yields of heavier products containing higher shares of sulphur and nitrogen compounds.

The influence of feedstock pretreatment severity in catalytic cracking and the reactor temperature on cracking gasoline composition and sulphur quantity in liquid cracking product in MAT-system, is shown in Table 6. Catalytic cracking process renders reactions of hydrogen transition which are exothermal which at higher reactor temperatures show lower activity, thus reducing the share of overall paraffines, and increasing the share of olefinic hydrocarbons in cracking gasoline composition, as shown in figures 5, 6, 7.

In the structure of cracking gasoline paraffinic fraction itself, the reactor temperature increasing indicates evident reduction of iso-parrafine yield, and small increase of n-paraffine yield, resulting in overall decrease of paraffinic hydrocarbons yield. The reduction of iso-paraffinic hydrocarbons was provoked by reactor temperature rising caused by weakening of influence of exothermal reactions of isomerization.

If we follow the dependability of paraffinic and oleofinic hydrocarbons share in cracking gasoline composition on feedstock pretreatment severity in catalytic cracking, it can be observed that paraffinic share increases with severity of feedstock pretreating, while the share of olefinic hydrocarbons is reduced in cracking gasoline composition, as a result of feedstock hydrocracking.

In above case it may be observed that n-paraffine and iso-paraffine shares in gasoline depend on feedstock pretreatment severity for catalytic cracking. With increased pretreatment severity the yield of iso-paraffine is increased, and n-paraffine yield decreased. As n-paraffines are octane depressors explicitely, iso-paraffines are desirable octane components, the positive influence of hydrocracking gasoline pretreatment severity is evident, particularly in catalytic cracking by application of lower reactor temperatures.

Naphtenic hydrocarbons share in FCC gasoline decreases with reactor temperature increase, and by increase of feedstock pretreatment severity in the FCC process, as shown in figure 8. In catalytic cracking naphtenic hydrocarbons could be developed from olefine cycling. Since FCC gasoline composition naphtenics share is mostly influenced by hydrodesulphurized and mildly cracked feedstock, its physical and chemical properties reveal low share of naphtenic hydrocarbons, bringing to the conclusion that the major cracking gasoline naphtenics share is in FCC gasoline composition derived from olefinic cycling. As the share of olefinic hydrocarbons in motor gasoline composition represents a limiting parameter (in the EU since 2000, max. 18 vol.% has been permitted annually, and for 2005 the restriction has not been agreed upon yet), low reactor temperatures should be applied in catalytic cracking, in case we wish to reduce the olefines share in FCC gasoline composition. Aromatic hydrocarbons in FCC gasoline composition could originate from aromatic hydrocarbons feedstock side chains cracking, forming unsubstituted aromates, or from aromatic feedstock transalkylation, forming aromates with alkyl chains different from the initial aromate. Aromatic hydrocarbons could originate from dehydrogenated naphtenes.

In the figure 9 it is shown that reactor temperature increase is enhancing aromatic hydrocarbon share in FCC gasoline composition, as cracking and dehydrogenating reactions are endotermic reactions, preferring higher reactor temperatures. At the same time, the share of aromatic hydrocarbons in FCC gasoline composition is reduced with increased feedstock pretreatment severity. It is due to the fact that feedstock hydrodesulphurization and mild hydrocracking supports hydrogenation of aromatic hydrocarbons containing sulphur, nitrogen and oxygen atoms, forming relevant paraffinic hydrocarbons with hydrogen sulfide, ammonia and water. Therefore the share of aromatics in pretreated feedstock is considerably lower than their share in not-treated feedstock, affecting the share of aromatics in FCC gasoline composition. Since aromatic hydrocarbons are the most important octane components in cracking gasoline, surely the increase of feedstock pretreatment severity will have negative influence on octane number derived for cracking gasoline.

As a consequence of presently limited analitical equipment, the determination of sulphur quantities in cracking gasoline was not possible, and it was determined from overall liquid cracking product in the MAT-system. As illustrated in figure 10, liquid cracking product sulphur is slowly decreasing with the increase of reactor temperature, which favours cracking of flatchain and cyclic compounds containing sulphur atom, forming relevant paraffine and hydrogen sulfide.

Figure 10 shows a evident decrease of sulphur quantity in liquid cracking product influenced by FCC feedstock pretreatment severity. In such a way cracking of liquid product from hydrodesulphurized cracked feedstock, in relation to reactor temperature, contains 430-640 max. ppm of sulphur, and liquid cracking product from hydrodesulphurized and mildly cracked feedstock contains 80-110 max. ppm of sulphur, while liquid cracking product from mild hydrocracking feedstock without pretreatment contains 610-700 max. ppm of sulphur. If we wish to maintain the quantity of cracking gasoline to be mixed into motor gasoline compositions (about 35 vol.%), it has been confirmed that for meeting specifications to be enforced in the EU in 2005, cracking gasoline may have max. 135 max. ppm of sulphur. This criteria in our case by no means is adequate for FCC gasoline from catalytic cracking desulphurized and mild hydrocracked feedstock, and most probably FCC gasoline from cracking of hydrodesulphurized mildly hydrocracked feedstock obtained at higher reactor temperatures. Cracking gasoline from feedstock treated only by mild hydrocracking is not going to meet the mentioned specifications.

5. CONCLUSION

From illustrated published references and obtained experimental results the following conclusions could be brought referring to the theme of feedstock pretreatment severity influence on catalytic cracking yields and sulphur quantity in catalytic cracking products:

- Feedstock hydrocracking increased the share of paraffinic hydrocarbons by transformation of mostly naphtenic, and less aromatic hydrocarbons, what significantly enhances crackability reflected in increased conversion.
- Catalytic cracking of hydrodesulphurized feedstock, carried out in the MAT-system, increased yield of gasoline amounting to 5-6 max.%, while catalytic cracking of hydrodesulphurized and mild hydrocracked feedstock rendered higher yield of about 10 max.% of cracking gasoline than with nonpretreated feedstock cracking.
- Simultaneously, the increased cracking gasoline yield brings to the reduction of light and heavy cycle oil, and coke.
- The influence of catalytic cracking feedstock pretreatment severity, is reflected in increased share of iso-paraffinic and naphtenic hydrocarbons in cracking gasoline composition, and in the reduction of olefinic and aromatic hydrocarbons. Catalytic cracking process conditions should be chosen so that the decreased octane number caused by the reduced share of aromatic hydrocarbons in cracking gasoline, will be compensated by the increased yield of iso-paraffines.
- The forthcoming specifications referring to the quantity of sulphur in motor gasolines, to be enforced by the EU in 2005, will be by all means met by the admixture of unchanged quantities of cracking gasoline produced from hydrodesulphurized and mildly hydrocracked feedstock, and most probably by the admixture of gasoline obtained from hydrodesulphurized feedstock on higher reactor temperatures. It will not be possible to satisfy requirements by admixture of gasoline from the feedstock pretreated only by a mild hydrocracking.

- Resuming all previously stated facts, it is evident that FCC feedstock pretreatment is not a cost and expense favouring option, for the refineries, indispensable for production of motor fuels in compliance with the anticipated specifications, but a better feedstock valorization is achieved by catalytic cracking feedstock pretreatment, what significantly increases cost-efficiency of the refineries based on fluid catalytic cracking.

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665.644.42-948 FCC fluidkatalitički kreking	FCC fluid catalytic cracking
.001.53 laboratorijsko istraživanje procesa	process laboratory research
544.478.1 MAT test mikroaktivnosti FCC katalizatora	MAT FCC microactivity catalyst test
665.733.5.033.52 sadržaj sumpora u motornom benzinu	motor gasoline sulphur content
351.777 (4) zahjevi ograničenja emisije sumpora Europske Zajednice	sulphur emission reduction requirements EU

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