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UTJECAJ OŠTRINE RADA KATALITIČKOG REFORMINGA NA TRAJANJE CIKLUSA I KVALITETU PROIZVODA U RAFINERIJI NAFTE RIJEKA

Sažetak

Za oktanski broj reformata od 99 jedinica, smanjenje protoka sirovine s projektnih 90 m^3*/h na 75 m*^{3}*/h ima za posljedicu sniženje Start of Run ulazne reaktorske temperature a 515,2 na 511℃ uz omjer vodika nasuprot ugljikovodicima 7,3: 1 i 23 bara na visokotlačnom separatoru Platforminga 2. Poznavajući maksimalne ulazne reaktorske temperature od oko 528℃ za postojeći tip katalizatora na Platformingu 2, proizlazi da se time temperaturno područje iskoristivosti katalizatora povećava s 12,8 na 17,1℃. Na taj način se od 116 dana ciklusa dolazi do prihvatljivije duljine ciklusa od 198 dana. Ovakva duljina ciklusa omogućava dvije regeneracije katalizatora godišnje.*

Iako Platforming 2 danas radi pod reaktorskim tlakom od 21 do 24 bara, zbog sljedljivosti podataka, za proračun je uzeta konstantna vrijednost tlaka recirkulirajućeg plina. Ne treba zaboraviti da svaka promjena u sastavu sirovine može uzrokovati nepredvidive promjene volumne koncentracije vodika u recirkulirajućem plinu odnosno varijacije u računsko određenoj vrijednosti trajanja ciklusa reforming katalizatora.

Duljina ciklusa od približno godinu dana a oktanskom vrijednošću reformata od 99 jedinica mogla bi se postići spuštanjem kapaciteta svježe šarže ispod 65 m3/h. Proces katalitičkog reformiranja na postrojenju Platforming 2 u RNR bi s kapacitetom od 62,5 m3/h svježe sirovine, omjerom H_2*/HC>9 omogućio duljinu ciklusa katalizatora od 357 dana.*

Uvod

Platinski katalizatori nove generacije su sve djelotvorniji i kreiraju se sukladno željenim produktima reformiranja benzina. Ipak, pogrešno je misliti da se samo razvojem novih katalizatora bez dodatnih preinaka na postojećim polu-regenerativnim postrojenjima može povećati trajanje ciklusa katalizatora na većoj oštrini rada.

Glavna ograničenja za to su masa katalizatora i njegova distribucija u procesnim reaktorima te snaga kompresora za recirkulirajući plin. Stoga preinaka polu-regenerativnog postrojenja danas uglavnom podrazumijeva ugradnju dodatnog reaktora kao posljednjeg u nizu[8]. Preinaka u proces reforminga cikličkog tipa (katalizator u svakom reaktoru se može neovisno regenerirati dok su ostali reaktori u radu) uglavnom je skupa i teško izvodiva. Jeftiniji način za povećanje trajanja ciklusa, razmatran i za Platforming 2, promjena je dizajna unutarnjih dijelova reaktora s ciljem povećanja aktivne mase katalizatora (texicap).

Postrojenje Platforming 2 tvrtke UOP, u Rafineriji nafte Rijeka je proces polu-regenerativnog tipa s tri reaktora. Izgrađeno je 1970. god. s bitnim parametrima rada procesa: tlak na visokotlačnom separatoru od 27-28 bara, optimalni protok sirovine od 90 m^3/h, zahtijevani oktanski broj reformata od 92-93 uz njegov iscrpak od oko 75 mas%[3]. Ti parametri su bili direktna posljedica tadašnjeg stupnja tehnologije platinskih katalizatora kao i tadašnjih karakteristika automobilskih motora (niži omjer kompresije). 1984. godine izvršena je modifikacija postrojenja Platforming 2 kojom se omogućio njegov rad na znatno nižem tlaku od projektnog (do 17 bara na separatoru visokog tlaka)[7]. Niži tlak promovira korisne reakcije reformiranja ugljikovodika za istu temperaturu slojeva katalizatora. Time su se omogućili i veći iscrpci reformiranog benzina, te veće količine vodika za rad sekundarnih procesa.

Usporedna nepoželjna posljedica nižeg tlaka u procesnim reaktorima je pojačano koksiranje katalizatora odnosno njegov kraći ciklus.

Utjecaj procesnih parametara na trajanje ciklusa

U Rafineriji nafte Rijeka trajanje ciklusa katalizatora Platforminga 2 obično izražavamo u danima rada procesa, dok omjer svježe sirovine po jedinici mase katalizatora koristimo za dodatnu indikaciju stanja katalizatora (parametar života katalizatora)[2].

Da bi se mogao prikazati utjecaj oštrog načina rada Katalitičkog reforminga na katalitički aktivne komponente te kvalitetu i kvantitetu produkata, treba definirati pojam ”oštrine” rada.

Procesne varijable neophodne za definiranje oštrine rada procesa su[1, 2]:

1. Tip katalizatora.
2. Tlak u reaktoru.
3. Temperatura u reaktoru.
4. Prostorna brzina (kapacitet).

5. Parcijalni tlak vodika ili H_2/HC omjer.
6. Kvaliteta sirovine.

Osim tipa katalizatora ovo su neovisne varijable jer se svaka od njih neovisno o drugim varijablama može podesiti, koliko god dopuštaju karakteristike opreme. Za podešavanje neovisnih varijabli mjerodavne su samo performance rada postrojenja[2]:

1. Prinos produkta.
2. Kvalitet produkta (IOB).
3. Trajanje ciklusa-Katalitička stabilnost.

Oštrinu rada Katalitičkog reforminga u Rafineriji nafte Rijeka prvenstveno uvjetuje i ograničava dizajn samog postrojenja Platforminga 2. To se prije svega odnosi na željeni kapacitet rada postrojenja, odnosno trajanje ciklusa. Postojeći tip katalizatora Platforminga 2 je bimetalni Pt-Re katalizator novije generacije i nikako nije ograničavajući faktor željenog režima rada.

Svi današnji reforming katalizatori posjeduju dvije ili tri metalno-aktivne komponente na kloriranoj gama-alumini (oko 99% mase katalizatora) kao nosiocu[8]. To ih čini prilično prilagodljivim za sve procese reformiranja benzina. Pri tome se njihova prilagodljivost velikom području radnog tlaka u procesnim reaktorima kreće od 7 do 40 bara.

Mehanizam djelovanja platinskih katalizatora na reakcije reformiranja je uglavnom poznat i općenito prihvaćen. Iako je vrsta katalizatora, njegova priprema za vrijeme regeneracije i reaktivacije jako bitna (razina klorida, distribucija metala), mogli bismo reći čak i presudna, u ovom radu neće biti previše riječi o tome.

Termin oštrine rada direktno je povezan sa zahtjevima za željenim oktanskim brojem reformata uz zadržavanje njegovog željenog iscrpka (C_5+). Oštrina rada je također povezana i sa brzinom relativne deaktivacije katalizatora koja iziskuje povećanje ulaznih reaktorskih temperatura za zadržavanje željene razine oktanskog broja[2]. Veća oštrina rada uzrok je ubrzanom gubitku aktivnosti i selektivnosti katalizatora kada se smanjuje iscrpak C5+ reformata i vodika naročito na kraju ciklusa kada termički reakcijski mehanizam nadvladava katalitički.

Općenito, povećanje zahtjeva za "oktanima" u reformatu, veće prostorne brzine, smanjenje tlaka u reaktorskoj sekciji, niži indeks cikličkog sadržaja sirovine, visok kraj destilacije sirovine povećavaju oštrinu rada procesa i ubrzavaju nastajanje koksa[1].

Posljedica povećane oštrine je i niži omjer H_2/HC koji je uvjetovan i dizajnom postrojenja. Zbog toga izbor katalizatora uvijek treba pratiti procesne uvjete, tj. dizajn samog postrojenja Katalitičkog reforminga.

Ograničenja postojećeg dizajna Platforminga 2

Većina rasprava o Platforming procesu razmatraju tlak kao temeljnu varijablu procesa[1,2,6], što sa stajališta promoviranja korisnih reakcija reformiranja i jest točno. Međutim, budući da postojeći katalizator nije ograničenje oštrijem režimu rada Platforminga 2 u Rafineriji nafte Rijeka, rad i trajanje ciklusa Platforming procesa najviše ovisi o karakteristikama visokotlačnog sustava postrojenja. Zbog toga se problem kapaciteta javlja kao najveće ograničenje stabilnosti katalizatora u procesnim reaktorima.

Ograničenje većem trajanju ciklusa, prvenstveno se odnosi na volumen procesnih reaktora tj. na masu katalizatora u procesnim reaktorima. Volumen sva tri reaktora dovoljan je za smještaj oko 43900 kg platina-renij reforming katalizatora dense loading metodom.

Projektni parametri postrojenja Platforming 2 zahtijevali su nisku temperaturu kombinirane šarže na početku ciklusa. Posljedica toga bilo je veliko temperaturno područje iskoristivosti katalizatora. Uz nisku brzini mjesečne relativne deaktivacije ispod 3℃, ovakav način rada Platforminga 2 omogućavao je ciklus katalizatora i preko godine dana. Niska oštrina i mali opseg reakcija reformiranja dopuštao je temperaturu na visokotlačnom separatoru i do 40℃. Omjer H_2/HC lako se mogao nadomjestiti pojačanjem rada turbokompresora, a net-separator plin bogat vodikom u to vrijeme nije promatran kao jedan od značajnijih produkata reformiranja ugljikovodika.

Današnji zahtjevi za većim oktanskim brojem reformiranog benzina (99-100) prvenstveno uvjetuju veće temperature kombinirane sirovine u reaktore na početku ciklusa (SOR WAIT). Time se smanjuje temperaturno područje ”iskoristivosti” katalizatora. Samim tim ubrzava se i relativna deaktivacija katalitički aktivnih komponenata[5].

Bitna posljedica veće oštrine rada je veći opseg svih reakcija reformiranja. Budući da projektni kapacitet zbog zadovoljavanja omjera H_2/HC zahtijeva projektni tlak u visokotlačnom sustavu postrojenja (nedovoljna snaga kompresora), dolazi do favoriziranja reakcija hidrokrekinga. Time dolazi do smanjenja udjela vodika u kombiniranoj sirovini što dodatno skraćuje ciklus katalizatora.

Zadovoljenje omjera H_2/HC podizanjem tlaka u visokotlačnom sustavu uzrok je daljnem zahtjevu za rast ulaznih reaktorskih temperatura i smanjenju udjela vodika u proizvedenom plinu Platforminga 2. Istina, manji udio vodika u recirkulirajućem plinu dovodi do manjeg porasta specifične topline recirkulirajućeg plina što pridonosi većoj količini topline za endotermne reakcije, ali i ubrzanim formiranjem depozita koksa na katalizatoru.

Boljim hlađenjem na visokotlačnom separatoru može se u manjem opsegu povećati udio vodika u net-separator plinu i neznatno povećati omjer H_2/HC. Ipak, s projektnim masenim protokom reaktorskog efluenta, uz njegovu pripadajuću izvanprojektnu temperaturu, javlja se problem nedovoljne kondenzacije težih ugljikovodika na visokotlačnom separatoru Platforminga 2.

Smanjivanjem pak tlaka u reaktorskoj sekciji dobiva se veći opseg odvijanja željenih reakcija reformiranja ugljikovodika (dehidrogenacija, dehidrociklizacija) uz blagi pad Start of Run temperature kombinirane sirovine i porast udjela vodika u recirkulirajućem plinu.

Međutim, smanjenjem tlaka, smanjuje se i snaga kompresora za recirkulirajući plin, što postaje ograničavajući faktor reformiranju projektnog protoka sirovine na nižem tlaku. Protok kombinirane sirovine tada pada na račun manjeg odnosa H_2/HC, što je direktno povezano s niskim parcijalnim tlakom vodika odnosno skraćenjem ciklusa.

Manjim masenim protokom kombinirane šarže u reaktorsku sekciju, pada potreba za većim količinama topline na prvom prolazu procesne peći. Međutim, veliki opseg endotermnih reakcija tada dovodi do zahtjeva za većim količinama topline na ulazu u drugi i treći reaktor. Time postaje upitan ukupni kapacitet procesne peći.

Trajanje ciklusa kao funkcija SOR WAIT

Mjera relativne deaktivacije je razlika prosječne ulazne reaktorske temperature i proračunom utvrđene Start of Run temperature kombinirane sirovine[1,2]. Uz dobru pripremu katalizatora za vrijeme njegove reaktivacije, brzina relativne deaktivacije, posljedica je samo oštrine rada procesa. Veća oštrina rada procesa zahtijeva veću Start of Run temperaturu kombinirane sirovine. Poznavajući maksimalnu ulaznu reaktorsku temperaturu i Start of Run temperaturu može se odrediti područje temperaturne iskoristivosti katalizatora odnosno približno trajanje ciklusa.

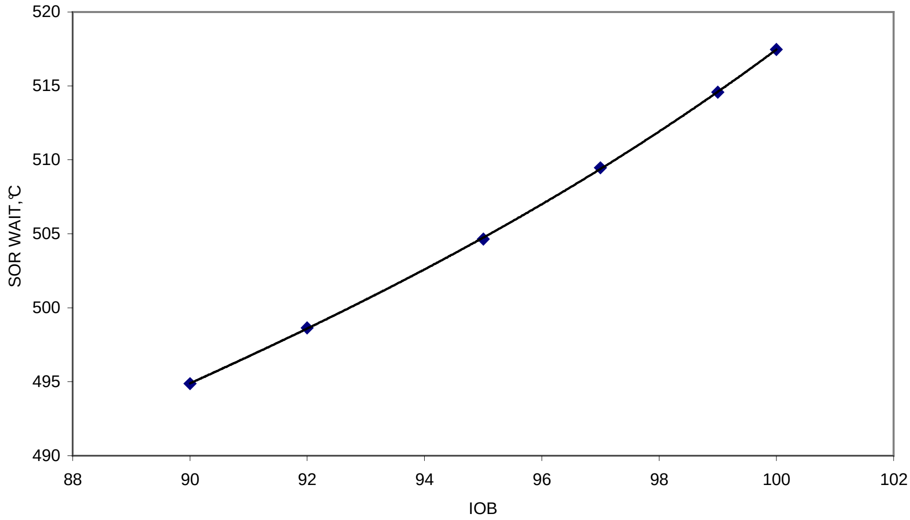
SOR WAIT (Start of Run Weighted Average Inlet Temperature) je ona temperatura kombinirane sirovine, koju novi katalizator zahtijeva za zadani oktanski broj reformiranog benzina na početku ciklusa. Ona ovisi o sljedećim bitnim parametrima[2,3]:

1. Oktanski broj reformata (IOB.)
2. Maseni protok kombinirane sirovine (prostorna brzina, omjer H_2/HC).
3. Tlak u reaktorskoj sekciji.
4. Sastav sirovine (vrijednost cikličkog indexa).
5. Razina klorida i stupanj dispergiranosti metala.

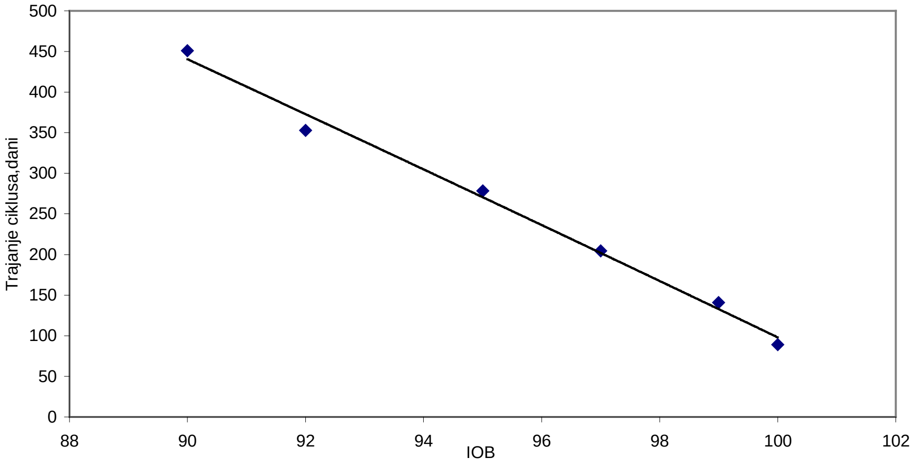
Na slikama/dijagramima je prikazana funkcija duljine ciklusa s kapacitetom Platforminga 2 te ovisnost SOR WAIT-a o količini kombinirane sirovine i vrijednosti IOB-a. Baza za njihovo definiranje su podaci proizvođača katalizatora s njegovih pilot-postrojenja[2] te karakteristike i procesni podaci postrojenja Platforming 2 u RN Rijeka[1,3,6].

Zahtjevi za većim oktanskim brojem reformata prvenstveno uvjetuju veću vrijednost SOR WAIT, odnosno veće temperature kombinirane šarže na početku ciklusa. Time se smanjuje područje temperaturne iskoristivosti katalizatora, te pojačavaju neželjene reakcije hidrokrekinga uz smanjenje iscrpka vodika. Svi efekti visokog oktanskog broja reformata ubrzavaju gubitak aktivnosti, tj. smanjuju trajanje ciklusa reforming katalizatora. Porast oktanskog broja reformata od 92 na 100 za projektni protok šarže zahtijeva povišenje Start of Run temperature kombinirane šarže za 18,9℃ (slika 1). Osim toga i veća brzina deaktivacije pri višim oktanskim brojevima reformata, osobito nakon dvije trećine ciklusa (znatno preko 4℃ za mjesec dana rada), povod je kraćem ciklusu katalizatora od oko 90 dana (slika 2).

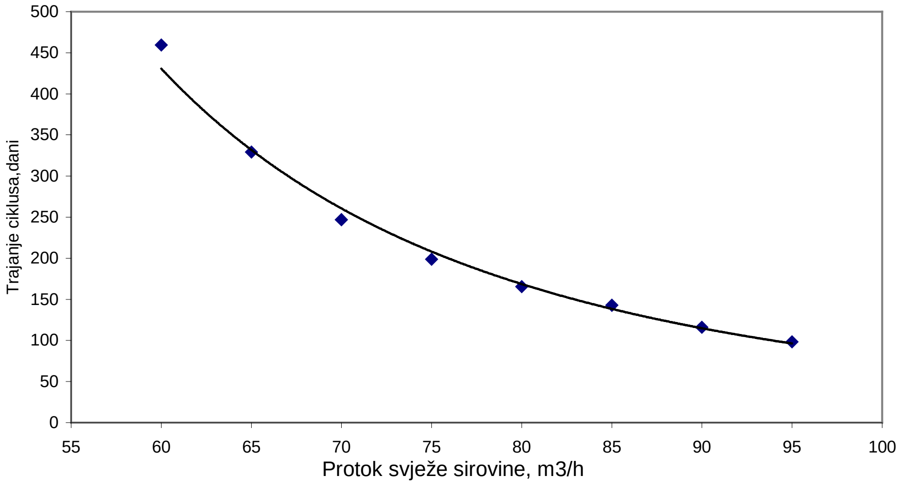
Slika 1: Ovisnost vrijednosti SOR WAIT o istraživačkom oktanskom broju reformata Platforminga 2
Figure 1: SOR WAIT value dependence on the Platforming 2 reformate RON



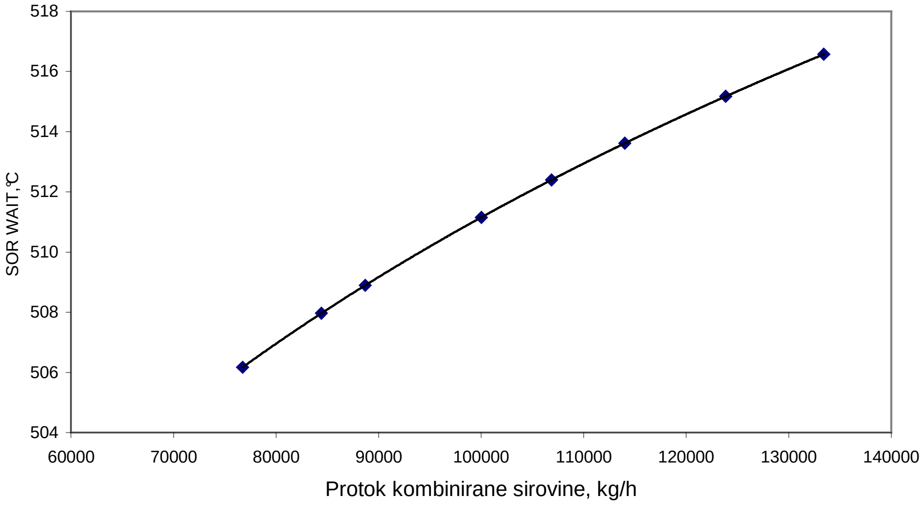
Slika 2: Ovisnost trajanja ciklusa o istraživačkom oktanskom broju reformata Platforminga 2
Figure 2: Cycle duration dependence on the Platforming 2 reformate RON



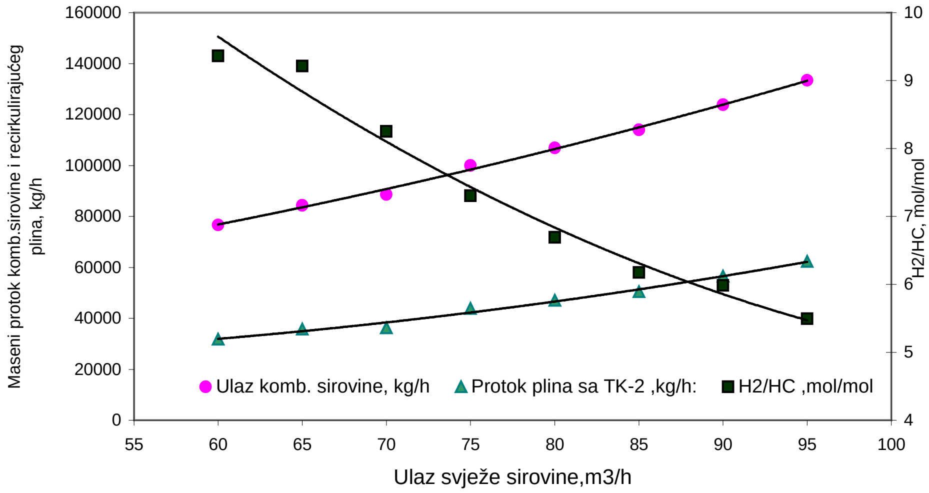
Slika 3: Ovisnost trajanja ciklusa o protoku svježe sirovine Platforminga 2
Figure 3: Cycle duration dependence on the Platforming 2 fresh charge flow



Slika 4: Ovisnost SOR WAIT o masenom protoku kombinirane sirovine
Figure 4: SOR WAIT dependence on the combined charge mass flow



Slika 5: Ovisnost protoka kombinirane sirovine i recirkulirajućeg plina te omjera H_2/HC o protoku svježe sirovine
Figure 5: Dependence of the combined charge and recycle gas flow and the H_2/HC ratio on the fresh charge flow

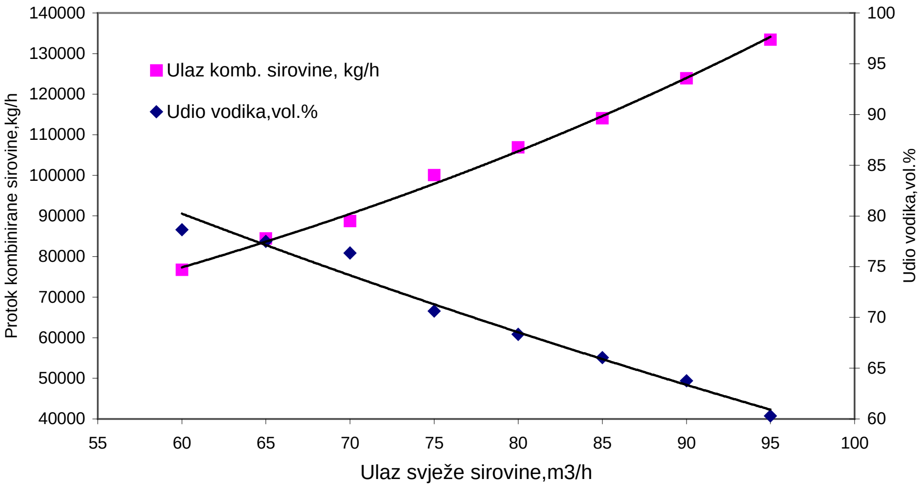


Veće prostorne brzine svježe sirovine znače i veći maseni protok kombinirane sirovine kroz masu katalizatora što je direktan uzrok njegovom kraćem ciklusu. Na slici 3 prikazana je ovisnost trajanja ciklusa o volumnom protoku svježe sirovine. Posljedica je potreba za većim temperaturama kombinirane sirovine na ulazu u reaktorsku sekciju (slika 4). Dakle, iako zadržavamo isti omjer vodika naspram ugljikovodika, povećanjem mase smanjuje se kontakt sirovine s katalizatorom što zahtijeva povećanje ulaznih reaktorskih temperatura za zadanu oktansku vrijednost.

Količina kombinirane sirovine ovisi i o omjeru H_2/HC. Na H_2/HC omjer najveći utjecaj ima promjena protoka svježe sirovine. Smanjenje omjera vodika naspram ugljikovodika implicira povećanje protoka recirkulirajućeg plina kroz reaktorsku sekciju (slika 5). Veći udio vodika u kombiniranoj sirovini smanjuje pokrivenost metalne komponente katalizatora ugljikovodicima, čime se smanjuje i gubitak njegove aktivnosti[8]. Manji udio vodika u recirkulaciji uz istu količinu ugljikovodične sirovine zahtijeva veću količinu recirkulirajućeg plina za održavanje omjera H_2/HC (slika 6).

Tlak u reaktorskoj sekciji ima utjecaj na opseg željenih reakcija reformiranja i udio vodika u recirkulirajućem plinu. Niži tlak za razliku od ostalih parametara smanjuje vrijednost SOR WAIT, ali i pokrivenost metalne komponente vodikom, što je razlog bržem formiranju depozita koksa na površini katalizatora. Zbog sljedljivosti podataka, za proračune su uzete konstantne vrijednosti tlaka u posljednjem reaktoru.

Slika 6: Ovisnost protoka kombinirane sirovine i volumnog udjela vodika u recirkulirajućem plinu o protoku svježe sirovine
Figure 6: Dependence of the combined charge flow and hydrogen volume share in the recycle gas on the fresh charge flow



U Rafineriji nafte Rijeka tipična sirovina Platforming procesa je frakcija nafte 80-180℃ s indeksom cikličkog sadržaja šarže (A+0,85N) između vrijednosti 34 i 36 (REB, Sirija-light). Manja vrijednost indeksa cikličkog sadržaja sirovine, zahtijeva njenu veću temperaturu prije kontakta sa katalizatorom za ostale iste procesne parametre. Za prikaz funkcija SOR WAIT-parametri procesa-trajanje ciklusa uzeta je konstantna vrijednost cikličkog indeksa od 34,6. Srednja točka destilacije sirovine Platforming procesa u Rafineriji nafte Rijeka, obično se kreće oko vrijednosti 127℃.

Koncentracija klorida na katalizatoru utječe na vrijednost IOB reformiranog benzina. Kako se s oktanskim brojem mijenja i vrijednost SOR temperature kombinirane sirovine, i koncentracija klorida ima izravan utjecaj na izgled krivulje relativne deaktivacije[4]. Kako koncentracija klorida i omjer H2O/HCl nisu predmet ovog rada, pretpostavljen je nivo klorida na katalizatoru u okviru optimalnog područja (0,9-1,1% mas.)[2].

U tablicama 1 i 2 prikazani su omjeri bitnijih parametara Platforminga 2 te njima odgovarajuće proračunate duljine ciklusa katalizatora. Ovi podaci se odnose na postojeći tip katalizatora Platforminga 2[2]. Manja odstupanja od ovih podataka mogu se dogoditi sa svakom promjenom sastava šarže koja za posljedicu ima promjenu kemizma reformiranja ugljikovodika.

Tablica 1: Parametri procesa i trajanje ciklusa katalizatora s promjenom kapaciteta

Kapacitet, m3/h	90	75	65
Gustoća sirovine, kg/dm3	0,7480	0,7480	0,7480
Istraživački oktanski broj (IOB)	99	99	99
Maseni protok sirovine, kg/h	67320	56100	48620
Prostorna brzina (WHSV), h^{-1}	1,533	1,278	1,108
Područje destilacije,°C	80-180	80-180	80-180
A+0,85N	34,6	34,6	34,6
Omjer H$_2$/HC, mol/mol	6,17	7,31	8,89
Udio vodika u rec.plinu, vol.%	63,75	70,63	78,65
Mas. protok recirkulirajućeg plina, kg/h	56546,6	43921,7	35797,4
Tlak recirkulirajućeg plina, bar	31	31	31
Maseni protok kombinirane sirovine, kg/h	123866,6	100021,7	84417,4
Tlak na ulazu u mjerodavni reaktor, bar	29	29	29
SOR WAIT,°C	515,2	510,9	508,0
Predviđeno trajanje ciklusa u danima rada	116,0	198,8	329,2

Tablica 2: Parametri procesa i trajanja ciklusa katalizatora s promjenom IOB reformata

Kapacitet, m3/h	90	90	90
Gustoća sirovine, kg/dm3	0,7480	0,7480	0,7480
Istraživački oktanski broj (IOB)	100	97	92
Maseni protok sirovine, kg/h	67320	67320	67320
Prostorna brzina (WHSV), h^{-1}	1,533	1,533	1,533
Područje destilacije,°C	80-180	80-180	80-180
A+0,85N	34,6	34,6	34,6
Omjer H$_2$/HC, mol/mol	5,98	6,57	7,73
Udio vodika u rec.plinu, vol.%	64,89	68,33	72,92
Mas. protok recirkulirajućeg plina, kg/h	54104,8	51925,2	50723,8
Tlak recirkulirajućeg plina, bar	31	31	31
Maseni protok kombinirane sirovine, kg/h	121424,8	119245,2	118043,8
Tlak na ulazu u mjerodavni reaktor, bar	29	29	29
SOR WAIT,°C	517,5	509,5	498,6
Predviđeno trajanje ciklusa u danima rada	89,1	204,7	352,8

Zaključak

Dulje trajanje ciklusa katalizatora na Platforming 2 može se postići:

1. smanjivanjem oštrine rada (spuštanje vrijednosti oktanskog broja reformata),
2. smanjivanjem kapaciteta na temelju zahtijevane oktanske vrijednosti reformata.

Masa katalizatora je konstantna i ne možemo je uzeti za parametar povećanja trajanja ciklusa, jer bi to s njegovom nepromijenjenom nasipnom gustoćom značilo mijenjanje dizajna cijelog postrojenja.

Veća masa katalizatora bi omogućila nižu vrijednost SOR WAIT, blaži pad deaktivacije te dulji život katalizatora na oštrijem režimu rada. Masa katalizatora i kapacitet su glavni faktori prostorne brzine. Prostorna brzina je (ne zanemarujući tlak i sastav sirovine) ipak glavni faktor početne zahtijevane temperature katalizatora za željeni oktanski broj reformata. Što je ona niža, temperaturno područje iskoristivosti katalizatora je veće.

Bez preinake postrojenja (ugradnja dodatnog reaktora s procesnom peći), ne možemo povećati masu katalizatora. Zbog zahtjeva za visokim oktanskim brojem reformiranog benzina ne možemo spustiti oštrinu rada procesa. Ono što možemo da bismo produljili ciklus, jest smanjenje prostorne brzine, tj. smanjenje protoka hidroobrađene sirovine u reaktorsku sekciju Platforminga 2.

Utjecaj povećane oštrine na produkte procesa ogleda se u većem opsegu reakcija dehidrogenacije i dehidrociklizacije, ali i hidrokrekiranja tijekom reformiranja benzina. To znači veće produciranje stabilnih aromatskih spojeva čime se smanjuje udio skupih oksigenata u finalnom namješavanju benzina za tržište.

Također treba obratiti pozornost i na čitav pool benzinskih komponenti, budući da će se u budućim specifikacijama ograničiti i sadržaj aromata.

Naravno da veća oštrina znači i veći pad prinosa reformiranog benzina na račun većeg prinosa ukapljenog naftnog plina. Međutim, određeni opseg reakcija hidrokrekinga je poželjan zbog koncentriranja nastalih aromatskih spojeva. Aromatski spojevi su ”nosioci oktana” u benzinu i njihova koncentracija je direktno proporcionalna izmjerenoj vrijednosti istraživačkog oktanskog broja. Veće produciranje aromata također je jedan od razloga za njihovu veću kondenzaciju u ireverzibilni oblik koksa na površini katalizatora.

THE IMPACT OF THE CATALYTIC REFORMING OPERATION SEVERITY ON CYCLE DURATION AND PRODUCT QUALITY AT THE RIJEKA OIL REFINERY

Abstract

For the reformate octane number of 99 the reduction of charge from the designed 90 m^3/h to 75 m^3/h results in the lowering of the Start of Run inlet reactor temperature from 515.2 to 511°C with a hydrogen/hydrocarbons share of 7.3: 1 and 23 bar at the high pressure separator. Knowing the maximal inlet reactor temperatures at Platforming 2 of around 528°C for the existing catalyst type, it turns out that the temperature range of catalyst usability goes up from 12.8 to 17.1°C. In this way, from 116 cycle days we come to a more acceptable cycle length of 198 days. Such cycle length enables two catalyst regenerations per year.

Although Platforming 2 today operates under reactor pressure from 21 to 24 bar, in order to be able to keep track of the data, for calculation presentation in Tables 1 and 2 we have taken a constant value of the recycle gas pressure. We should not forget that every change in charge composition may cause impredictable changes of the volumetric hydrogen concentration in the recycle gas i.e. variations in the calculated reforming catalyst life value.

Cycle duration of approximately one year with the reformate octane value of 99 units could be reached by the fresh charge capacity lowering below 65 m^3/h. The catalytic reforming process at the Platforming 2 plant at Rijeka Oil Refinery would, with the capacity of 62.5 m3/h of fresh charge, and a H_2/HC ratio >9, enable the catalyst cycle length of 357 days.

Introduction

Platinum catalysts of the new generation are becoming growingly efficient and are created in keeping with the desired gasoline reforming products. Still, it is wrong to think that only the development of new catalysts, without additional alterations of the existing semi-regenerative plants, may increase catalyst life at a higher operation severity.

The greatest limitations in this respect are the catalyst mass and its distribution in reactors, as well as the recycle gas compressor power. That is why the alteration of the semi-regenerative plant today mostly includes the building in of an additional reactor as the last one of the series. The alteration to a reforming process of a cyclical type (catalyst in every reactor may be regenerated independently while the other reactors are operative) is mostly expensive and difficult to achieve. A cheaper way of increasing cycle duration, considered also for Platforming 2, is modifying design of interior reactor parts with the purpose of increasing the catalyst's active mass (texicap).

The Platforming 2 plant at the Rijeka Oil Refinery, designed by UOP, is a semi-regenerative type process with three reactors. It was built in 1970 with the following significant process operation parameters: pressure on the high pressure separator from 27-28 bar, optimal charge flow of 90 m^3/h, required octane reformate number from 92-93, with its yield of about 75 mas.%. These parameters were the direct consequence of the then platinum catalysts technology level, as well as the automotive engine properties of that time (lower compression ratio). In 1984, a modification of the Platforming 2 plant was made, enabling its operation at a much lower pressure than the one envisaged by the original project (up to 17 bar at the high pressure separator). Lower pressure promotes useful reactions of hydrocarbon reforming for the same temperature of catalyst layers. This has enabled also higher yields of reformed gasoline, and higher volumes of higher purity hydrogen for the operation of secondary processes.

The accompanying undesirable consequence of lower pressure in process reactors is an increased catalyst coking i.e. its shorter life.

The impact of process parameters on cycle duration

At the Rijeka Oil Refinery, we usually express the Platforming 2 catalyst life in days of process operation, while the ratio of charge per catalyst mass unit is used for an additional indication of the catalyst's condition (catalyst's service life parameter).

In order to be able to present the impact of the severe operation mode of the catalytic reforming on the catalytically active components, as well as the quality and quantity of products, we should define the concept of "severity" of operation.

Process variables necessary for defining the severity of process operation are as follows:

1. Catalyst type
2. Reactor pressure
3. Reactor temperature
4. Space velocity (capacity)
5. Partial hydrogen pressure or H_2/HC ratio
6. Charge quality

Apart from catalyst type, these are independent variables because each one of them may be set independently of other variables, to the extent that the equipment properties allow. For the setting of independent variables, only the plant's operating performances count:

1. Product yield
2. Product quality (reformate octane number)
3. Cycle duration-catalytic stability (coke production)

The catalytic reforming severity of operation at the Rijeka Oil Refinery is both conditioned and limited primarily by the design itself of the Platforming 2 plant. This primarily refers to the desired plant operation capacity, i.e. cycle duration. The existing Platforming 2 catalyst type is the bimetal Pt-Re catalyst of a new generation and by no means represents the limiting factor of the desired operating regime.

All the present reforming catalysts have two or three metal-active components on a chlorinated gama-alumina (around 99 % of the catalyst mass) as the carrier. This makes them quite adjustable to all the gasoline reforming processes. Their adjustability to a wide range of operating pressure values in the process reactors ranges from 7 to 40 bar.

The mechanism of the platinum catalysts' activity on reforming reactions is mostly known and generally accepted. Although the catalyst type; its preparation during regeneration and reactivation, are very important (level of chlorides, distribution of metals), we could even say crucial, we shall not be discussing them much in the present paper.

The notion of severity of operation is directly associated with the requirements for desired reformate octane number, while maintaining its desired yield (C_5+). The severity of operation is also associated with the velocity of relative deactivation of the catalyst requiring increase of input reactor temperatures for maintaining the desired octane number level. Increased severity of operation is the cause of the catalyst's speedy loss of activity and selectivity when the yield of C5+ reformate and hydrogen decreases, - especially at the end of the cycle when the thermal reaction mechanism wins over that catalytic.

Generally speaking, increased requirements for "octanes" in the reformate, higher space velocities, pressure decrease in the reactor section, lower cyclic charge content index, high charge distillation end, increase the process operation severity i.e. speed up coke generation.

Increased severity results in lower H_2/HC ratio, conditioned also by plant design. That is why the catalyst choice must always follow the process conditions i.e. the design of the catalytic reforming plant itself.

Limitations of the existing Platforming 2 design

Most discussions of the platforming process consider pressure as the basic process variable, which is true from the viewpoint of promoting useful reactions of reforming. However, since the existing catalyst is no limitation to a more severe Platforming 2 operating regime at the Rijeka Oil Refinery, the operation and duration of the platforming process cycle are mostly dependent on the properties of the plant's high pressure system. That is why the issue of capacity appears as the greatest limitation of catalyst stability in process reactors.

The limitation to a longer cycle duration, refers primarily to the volume of process reactors i.e. to the catalyst mass in process reactors. The volume of all three reactors is sufficient for accommodating around 43,900 kg of platinum-renium reforming catalyst using the dense loading method.

Project parameters of the Platforming 2 plant have required a low temperature of the combined charge at the beginning of the cycle. This resulted in a large catalyst usability temperature area. At a low speed of the relative monthly deactivation below 3℃, such a mode of Platforming 2 operation enabled catalyst cycle of even over a year. Low severity and small volume of reforming reactions has permitted the temperature at the high pressure separator of up to 40℃ H_2/HC ratio could easily be substituted by increased turbo compressor operation, while the hydrogen rich net-separator gas was at the time not seen as one among the more significant hydrocarbon reforming products.

The present requirements for a higher reformed gasoline octane number (99-100) condition primarily higher temperatures of the combined charge at the reactors at the beginning of the cycle (SOR WAIT). This decreases the temperature range of catalyst ”usability”. This in turn speeds up the relative deactivation of catalytically active components.

An important consequence of higher severity of operation is the higher volume of all reforming reactions. Since the project capacity – due to the meeting of the H_2/HC ratio requirements – requires project pressure at the plant’s high pressure system (insufficient compressor power), hydrocracking reactions are being favoured. This in turn lowers the hydrocarbon share in the combined charge, thus additionally shortening the catalyst cycle.

The meeting of the H_2/HC ratio by increasing pressure in the high pressure system causes a further requirement for the increase of input reactor temperatures and yet another decrease in the purity of hydrogen in the gas produced at Platforming 2. True, decrease in hydrogen purity in the recycle gas leads to a lower increase of the recycle gas specific heat, contributing to a higher volume of heat for endothermal reactions, but also a speedy formation of coke deposit on the catalyst.

Better cooling at the high pressure separator may to a lesser extent increase hydrogen purity, as well as the H_2/HC ratio. Still, with the designed mass flow of the reactor effluent, with its pertaining out-of-design temperature, there is the issue of insufficient condensation of heavier hydrocarbons at the Platforming 2 high pressure separator.

By lowering pressure at the reactor section, we obtain a higher volume of the desired hydrocarbon reforming reactions (dehydrogenation, dehydrocycling), with a mild drop of the Start of Run temperature of the combined charge and increased degree of hydrogen purity in the recycle gas.

However, pressure lowering is accompanied by the lowering of power of the compressor for recycle gas, becoming a limiting factor for the reforming of the project charge volume at lower pressure. The flow of the input combined charge then drops at the cost of a lower H_2/HC ratio, which is directly associated with a low partial hydrogen pressure i.e. cycle shortening.

Lower mass flow of the combined charge in the reactor section decreases the need for higher heat volumes at the first process furnace passage. However, the great amount of endothermal reactions then leads to the requirement for higher heat volumes at the entrance to the second and the third reactor. This brings the total process furnace capacity in question.

Cycle duration as a function of SOR WAIT

The measure of the relative deactivation is the difference between the average input reactor temperature and the calculated Start of Run temperature of the combined charge. Assuming a good catalyst preparation during its reactivation, the relative deactivation velocity becomes the result of the process' severity of operation. Higher process' severity of operation requires a higher Start of Run temperature of the combined charge. Knowing the maximal inlet reactor temperature and Start of Run temperature, it is possible to define the area of the catalyst's temperature usability i.e. approximate cycle duration.

SOR WAIT (Start of Run Weighted Average Inlet Temperature) is the combined charge temperature required by the new catalyst for the given reformed gasoline octane number at the beginning of the cycle. It depends on the following significant parameters:

1. Reformate octane number (RON)
2. Combined charge mass flow (space velocity, H_2/HC ratio)
3. Pressure in the reactor section
4. Charge composition (the cyclic index value)
5. Chlorine level and metal dispersion degree.

The diagrams below show the cycle length function with the Platforming 2 capacity, and SOR WAIT dependence on the combined charge volume and RON value. The basis for their definition are the catalyst manufacturer data from his pilot-plants, and properties and process data of the Platforming 2 plant at the Rijeka Oil Refinery.

The requirements for a higher reformate octane number condition primarily a higher SOR WAIT value i.e. higher temperatures of the combined charge at the beginning of the cycle This decreases the temperature range of catalyst usability and increases the unwanted hydrocracking reactions with a reduced hydrogen yield. All the effects of the high reformate octane number speed up activity loss i.e. reduce the catalyst reforming cycle duration. The reformate octane number increase from 92 to 100 for the designed charge flow requires increase of Start of Run temperature of the combined charge by 18.9℃ (Figure 1). Also, the higher deactivation velocity at higher reformate octane numbers, especially after two thirds of the cycle (much over 4℃ for a month of operation), is the cause of the shorter catalyst cycle of around 90 days (Figure 2).

Higher space velocities of the charge also mean a higher mass flow of the combined charge through the catalyst mass, which is a direct cause of its shortened cycle. Figure 3 shows the dependence of cycle duration on the fresh charge volumetric flow. The result is the need for higher temperatures of the combined charge at the entrance to the reactor section (Figure 4). Thus, although we maintain the same hydrogen ratio with regard to hydrocarbons, by increasing the mass the contact of the charge with the catalyst is reduced, requiring the increase of inlet reactor temperatures for the given octane value.

The combined charge volume also depends on the H_2/HC ratio. The H_2/HC ratio is most influenced by the fresh charge flow change. Lowering of the hydrogen share with regard to hydrocarbon implies increased recycle gas flow through the reactor section (Figure 5). Higher hydrogen share in the combined charge lowers the coverage of the catalyst's metal component by hydrocarbons, thus reducing also the loss of its activity. Lower hydrogen share in recirculation with the same volume of hydrocarbon charge requires a higher volume of the recycle gas for maintaining the H_2/HC ratio (Figure 6).

The pressure in the reactor section impacts the desired reforming reactions and hydrogen share in the recycle gas. Lower pressure, unlike other parameters, reduces the SOR WAIT value, but also the coverage of the metal component by hydrogen, causing a faster coke deposit formation on catalyst surface. In order to be able to follow the data better, for calculations we have used constant pressure values in the last reactor.

At the Rijeka Oil Refinery, typical Platforming process charge is the 80-180℃ oil fraction with the cyclic charge content index (A+0.85N) between the values 34 and 36 (REB, Syrian-light). Lower value of the cyclic charge content index requires its higher temperature before the contact with the catalyst for other same process parameters. In order to present the SOR WAIT functions-process parameters-cycle duration we have taken a constant cyclic index value of 34.6. Medium distillation point of the Platforming process charge at Rijeka Oil Refinery is usually around 127℃.

Chloride concentration on the catalyst impacts the reformed gasoline RON value. Since, along with the octane number, the combined charge SOR temperature value also changes, chloride concentration has a direct impact on the appearance of the relative deactivation curve. Since chloride concentration and H_2O/HCl ratio are not the object of the present paper, we have assumed the chloride level on the catalyst within the optimal area (0.9-1.1% mas.).

Tables 1 and 2 present ratios of the more significant Platforming 2 parameters and their pertaining calculated catalyst cycle lengths. These data refer to the existing Platforming 2 catalyst type. Small aberrations from these data may occur with every charge composition change resulting in the change of the hydrocarbon reforming chemistry.

Table 1: Process parameters and catalyst cycle duration with a capacity change

Capacity, m3/h	90	75	65
Charge density, kg/dm3	0,7480	0,7480	0,7480
Research Octane Number (RON)	99	99	99
Mass charge flow, kg/h	67320	56100	48620
Space velocity (WHSV), h-1	1,533	1,278	1,108
Distillation range,°C	80-180	80-180	80-180
A+0.85N	34,6	34,6	34,6
H_2/HC ratio, mol/mol	6,17	7,31	8,89
Hydrogen share in rec.gas, vol.%	63,75	70,63	78,65
Mas. flow of recycle gas, kg/h	56546,6	43921,7	35797,4
Recycle gas pressure, bar	31	31	31
Combined charge mass flow, kg/h	123866,6	100021,7	84417,4
Pressure at the entrance into the competent reactor,bar	29	29	29
SOR WAIT,°C	515,2	510,9	508,0
Envisaged cycle duration in days of operation	116,0	198,8	329,2

Table 2: Process parameters and catalyst cycle duration with the reformate RON change

Capacity, m3/h	90	90	90
Charge density, kg/dm3	0,7480	0,7480	0,7480
Research Octane Number (RON)	100	97	92
Mass charge flow, kg/h	67320	67320	67320
Space velocity (WHSV), h-1	1,533	1,533	1,533
Distillation range,°C	80-180	80-180	80-180
A+0.85N	34,6	34,6	34,6
H_2/HC ratio, mol/mol	5,98	6,57	7,73
Hydrogen share in rec.gas, vol.%	64,89	68,33	72,92
Mas. flow of recycle gas, kg/h	54104,8	51925,2	50723,8
Recycle gas pressure, bar	31	31	31
Combined charge mass flow, kg/h	121424,8	119245,2	118043,8
Pressure at the entrance into the competent reactor,bar	29	29	29
SOR WAIT,°C	517,5	509,5	498,6
Envisaged cycle duration in days of operation	89,1	204,7	352,8

Conclusion

Longer catalyst cycle duration at Platforming 2 may be achieved:

1. By reducing severity of operation (lowering the reformate octane number value)
2. By capacity lowering based on the required reformate octane value.

Catalyst mass is constant and cannot be taken as parameter of cycle duration increase, because – given its unchanged pour-in density – it would mean changing the design of the entire plant.

Higher catalyst mass would enable a lower SOR WAIT value, milder deactivation drop, and longer catalyst's service life at a more severe operating regime. Catalyst mass and capacity are the main factors of space velocity. Space velocity is (without neglecting pressure and charge composition) still the main factor of the required inlet catalyst temperature for the desired reformate octane number. The lower it is, the higher the catalyst's temperature usability range.

Without reconstructing the plant (building in an additional reactor with the process furnace), we cannot increase catalyst mass. Due to requirements for a high octane number of the reformed gasoline, we cannot lower the process' severity of operation. What we can do in order to prolong the cycle is to reduce the space velocity i.e. the hydrotreated charge flow into the Platforming 2 reactor section.

The impact of increased severity on process products reflects in the higher volume of dehydrogenation and dehydrocycling reactions, but also that of hydrocracking during gasoline reforming. This means higher production of stable aromatic compounds, thus reducing the share of costly oxigenates in the final gasoline blending for the market.

Due attention should be paid also to the complete gasoline components pool, because future specifications will also limit the aromatics contents.

Of course, higher severity means also a higher decrease of the reformed gasoline yield at the expense of a higher LNG yield. However, a certain volume of hydrocracking reactions is desirable due to the concentration of generated aromatic compounds. Aromatic compounds are ”octane carriers” in gasoline and their concentration is directly proportional to the measured value of the Research Octane Number. Higher aromatics production is also one of the reasons for their higher condensation into irreversible form of coke on catalyst surface.

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665.644.442-947 oštrije vođenje platforminga	severe running of platforming
665.733.5 motorni benzin	motor gasoline
665.733.5.035.3 oktanski broj	octane number
.002.237 gledište poboljšanja kvalitete	viewpoint of quality improvement

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