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POVEĆANJE ČISTOĆE VODIKA APSORPCIJOM

Sažetak

Sukladno današnjim visokim ekološkim zahtjevima, procesi hidroobrade postaju prioritetni procesi prerade nafte. To se prije svega odnosi na sadržaj sumpora u gorivima što dovodi u pitanje opstanak mnogih prerađivača nafte. To je bio i glavni razlog za izgradnju novog postrojenja za HDS/BHK težih frakcija nafte u Rafineriji nafte Rijeka. Time su količine i čistoća vodika postali vrlo bitni parametri koji utječu na optimiranje rada rafinerije. O raspoloživosti dostatne količine i čistoće vodika ovisi ne samo iskorištenje procesa nego i zadovoljenje najstrožih zahtjeva na sadržaj sumpora u produktima.

U Rafineriji nafte Rijeka, kao i u mnogim drugim rafinerijama platforming proces je jedini proizvođač vodika. Čistoća vodika ovisno o procesnim parametrima u postojećim RNR platforming procesima kreće se od 65 do 75% vol. Budući da se pokazalo da je ta čistoća predstavljala znatno ograničenje za procese hidroobrade i hidrokrekinga, tražen je način za obogaćivanje ”net-separator plina” platforminga.

Rafinerijskim stručnjacima već odavno su poznati procesi proizvodnje čistog vodika iz lakših i težih frakcija nafte ili prirodnog plina. Međutim, izgradnja takvih procesa zahtijeva značajna dodatna ulaganja i vrijeme. Isto tose odnosi i za izgradnju poznatih tehnoloških procesa za pročišćavanje plinova bogatih vodikom. Navedene činjenice prisilile su nas da što hitnije pronađemo optimalno rješenje unutar rafinerije.

To je osim optimiranja rada platforming procesa rezultiralo i iskorištenjem dijela procesne opreme u svrhu novog načina pridobivanja vodika više čistoće u RNR.

Na osnovi idejnog rješenja izrađene su teoretske, tehnološke i tehničke podloge za realizaciju procesa pridobivanja vodika više *čistoće postupkom apsorpcije na koloni 17 C-1 koja je fizički u sklopu Tatoray procesa i ne koristi se više od 12 godina.*

Kolona 17 C-1 tehničk-tehnološki postaje apsorber na kojem se apsorbiraju lagani ugljikovodici iz "net-separator plina" proizvedenog na platformingu 2. Kao apsorbens u našem slučaju koristimo stabilizirani i ohlađeni platformat koji ima iznimno dobre apsorpcijske karakteristike.

Spajanjem kolone 17–C1 sa stabilizator kolonom platforminga 2, kolona za stabilizaciju je preuzela ulogu stripiranja apsorbiranih ugljikovodika iz apsorbensa (ohlađeni platformat) koji će se izdvajati kao suhi i tekući plin na vršnoj posudi kolone za stabilizaciju.

Uključivanje kolone za kontinuiranu apsorpciju u proces platforminga 2 imalo je višestruke pozitivne učinke.

1. *Postignut je glavni cilj, a to je obogaćivanje proizvedenog plina platforminga 2 na preko 83 % vol. vodika.*
2. *Istodobno, apsorbiranjem vrijednih ugljikovodika iz platformingovog plina (C_3 i C_4 ugljikovodici) značajno je povećan iscrpak tekućeg plina na samom postrojenju platforminga.*
3. *Čistoća plina od preko 83% vol. udjela vodika osigurala je rad i HDS i BHK postrojenja na maksimalnim kapacitetima i oštrinama, te pridobivanje optimalno kvalitetnih produkata.*
4. *HDS načinom rada pridobiva se na postrojenju maksimalna količina i kvaliteta plinskog ulja odnosno dizelskog goriva.*
5. *BHK načinom rada pridobiva se maksimalna količina i kvaliteta šarže za FCC postrojenje. Na FCC postrojenju preradom kvalitetno hidroobrađene šarže postižu se dodatni pozitivni učinci, a to su prvenstveno povećani iscrpci benzina, tekućeg plina i lakog katalitičkog ulja, na račun manje vrijednog dekantiranog ulja i suhog plina. Svi proizvodi FCC-a imaju minimalan sadržaj sumpora što se kao konačan pozitivan učinak reflektira u procesu namješavanja komercijalnih proizvoda.*

UVOD

Zahtjevi zaštite okoliša su danas sve više i zahtjevi tržišta, što je bio glavni razlog za investiranje i izgradnju novog postrojenja za desulfurizaciju težih frakcija nafte u Rafineriji nafte Rijeka. Godine 1997. pokrenuto je novo postrojenje za hidrodesulfurizaciju i blagi hidrokreking (HDS–BHK) tvrtke IFP (Institut Francais du Petrole). Zbog potrebe za širim rasponom ulazne šarže te što se tiče specifičnih gustoća, a i količine nepoželjnih spojeva u samoj šarži (prvenstveno, nezasićeni spojevi, sumporni i aromatski spojevi dušika, te spojevi teških metala) postrojenje je projektirano za dva načina rada: HDS i BHK. Time se htjela postići fleksibilnost postrojenja HDS–BHK, te manja osjetljivost na velike oscilacije u kvaliteti sirovine u Rafineriji nafte Rijeka.

HDS način rada je predviđen za hidrodesulfurizaciju smjese lakog plinskog ulja sa atmosferske destilacije nafte i lakog katalitičkog ulja (produkt FCC-a) čime se osigurava proizvodnja glavne komponente za namješavanje komercijalnih dizelskih goriva.

BHK način rada projektiran je za hidroobradu sirovine koja se sastoji od vakuum teškog i vakuum lakog plinskog ulja, a produkti su hidroobrađeni benzin i hidroobrađeno plinsko ulje te ostatak, što je sirovina za postrojenje fluid katalitičkog krekinga. Ovim načinom rada postrojenja znatno se optimizira proizvodnja bijelih produkata u Rafineriji nafte Rijeka te sam rad postrojenja fluid katalitičkog krekinga (lakše reakcije krekiranja u samom reaktoru) čiji produkti sadrže višestruko manje količine sumpora.

Već u prvom ciklusu rada postrojenja HDS–BHK utvrđen je nedostatak u čistoći vodika u njegovom recirkulirajućem plinu. Iako je prije pokretanja HDS-BHK postrojenja izvršena zamjena katalizatora na postrojenju platforminga 2, u svrhu pridobivanja većih količina i čistoće vodika, nisu postignuti očekivani rezultati. Kupnjom novih platforming katalizatora trebale su se omogućiti veće količine proizvedenog plina (make-up za HDS–BHK) koje bi omogućile minimalnu čistoću vodika u cirkulirajućem plinu postrojenja HDS–BHK od 73%.

Međutim, čistoća vodika, zbog oštrog režima rada platforming procesa, kvalitete prerađivane šarže te postupne deaktivacije katalizatora, nije zadovoljavala potrebe projektnih i procesnih uvjeta na postrojenju HDS-BHK. Treba istaknuti da su količine plina s postrojenja platforming 2 bile dostatne, ali je ipak glavno ograničenje bila čistoća vodika u recirkulirajućem plinu HDS-BHK postrojenja. Zbog svih navedenih razloga bio je ograničen kapacitet prerade HDS-BHK postrojenja u oba načina. Takva situacija apsolutno nije bila prihvatljiva u procesu optimiranja rada Rafinerije nafte Rijeka.

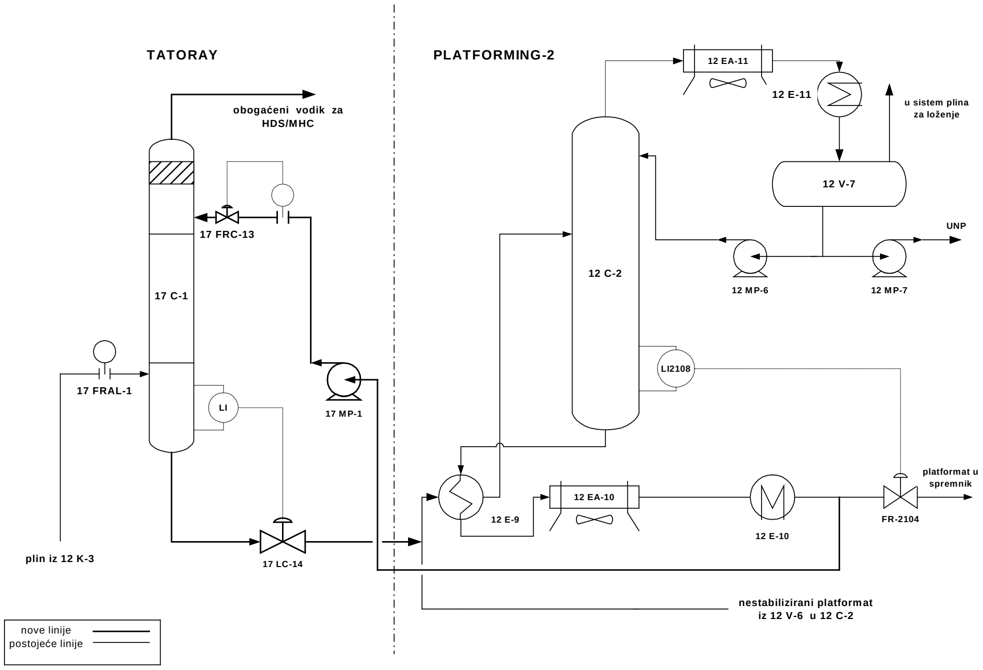
Kako je platforming proces jedini proizvođač vodika u rafineriji nafte Rijeka, sve aktivnosti usmjerene su ka pronalaženju prihvatljivog rješenja za povećanje čistoće proizvedenog vodika.

Spajanje apsorpcijske kolone s platformingom 2

Rafinerijskim stručnjacima već su odavno poznati procesi proizvodnje čistog vodika iz lakših i težih frakcija nafte ili prirodnog plina. Međutim, izgradnja takvih procesa zahtijeva značajna dodatna ulaganja i vrijeme. Isto to se odnosi i na izgradnju poznatih tehnoloških procesa za pročišćavanje plinova bogatih vodikom. Navedene činjenice prisilile su nas da što hitnije pronađemo optimalno rješenje unutar rafinerije.

Rješenje se našlo u pokretanju dijela sekcije za obogaćivanje vodika postrojenja Tatoray, kolone za kontinuiranu apsorpciju 17-C1.

Slika 1: Spajanje kolone 17–C1 s niskotlačnim sustavom postrojenja platforming 2
Figure 1: Connecting the 17–C1 column to the low pressure system of the Platforming 2 plant



obogaćeni vodik=enriched hydrogen
sistem plina za loženje=heating gas system
nove linije=new lines
postojeće linije=existing lines
platformat u spremnik=platformate to tankage
nestabilizirani platformat iz... u...=unstabilized platformate from...to...

Prvobitna namjena postrojenja Tatoray bila je hidrodealkilacija C7 aromata te je ono do 1990. godine radilo pod imenom Hydeal. Hydeal je imao sekciju za obogaćivanje svog cirkulirajućeg plina vodikom koju je sačinjavala kolona 17–C1 skupa sa striper kolonom 17–C2 koja je služila za stripiranje apsorbiranih ugljikovodika iz apsorbensa (toluen). Prenamjenom Hydeala u Tatoray kolona 17–C1 više nije radila kao apsorber, jer u procesu transalkilacije aromata potrošnja vodika je neznatna, tako da je make–up s platforminga 2 bio dovoljan.

Zbog nedostatka pojedinih dijelova opreme na stripperu apsorbensa, a naročito zbog nedostatka toplinske energije za stripiranje zasićenog apsorbensa, kolona 17–

C1 je spojena s niskotlačnim sustavom platforminga 2. Kao apsorbens iskorišten je ohlađeni i stabilizirani reformat (bez sadržaja C_4-), a stabilizacijska kolona platforminga 2 je preuzela ulogu stripiranja apsorbiranih ugljikovodika iz apsorbensa.

Time se osim povećanja čistoće vodika u make-up plinu za postrojenje HDS-BHK dobilo i povećanje iskorištenja ukapljenog naftnog plina na platformingu 2 njegovim većim izdvajanjem na vršnoj posudi stabilizacijske kolone.

Čistoća vodika ovisno o procesnim parametrima u postojećim RNR platforming procesima kreće se od 65 do 75% vol. Stavljanjem u funkciju apsorber kolone Tatoray procesa na tok make-up plina postrojenja HDS-BHK dobiva se povećanje koncentracije vodika i do preko 83% vol. Ovakvi efekti se postižu uz volumni protok i do12000 Nm3/h plina kroz apsorpcijsku kolonu 17-C1 što je 20 % više od njezinog projektnog kapaciteta.

Treba napomenuti da bez optimalnog rada platforminga 2, apsorpcija laganih ugljikovodika u platformat u koloni 17–C1 ne bi bila efikasna u postizanju dovoljno visokog parcijalnog tlaka vodika u make–up plinu za HDS-BHK. To se odnosi na neminovnu oštrinu rada platforminga 2, te projektne kapacitete njegovog niskotlačnog sustava (opterećenje stabilizacijske kolone i peći za njezino rebojliranje). Optimalan rad platforminga 2, osim oktanskog broja i količine reformata te količine tekućeg plina uzima i proizvedeni plin na visokotlačnom separatoru kao vrlo bitan produkt procesa.

Rekuperiranje C3 i C4 ugljikovodika

Standardni UOP semiregenerativni platforming proces ne predviđa obogaćivanje svog proizvedenog plina. Dosadašnje opće poznato rješenje za koncentriranje vodika koji se nalazi u smjesi s drugim plinovima su PSA sustavi (Pressure Swing Adsorption). PSA sustavi se obično koriste kao dopunski dio opreme nakon glavnog procesa proizvodnje vodika (Steam Reforming) i rade na principu adsorpcije plinova na čvrstom adsorbensu. Za razliku od drugih plinova, vodik se zbog svojih karakteristika ne adsorbira na procesnim uvjetima PSA sustava tako da se PSA procesom čistoća vodika u izlaznom plinu povećava na 99,99% vol. PSA sustavi se zbog svoje otpornosti na agresivne plinove osim finalizacije rada steam reforminga mogu koristiti i za koncentriranje vodika i iz drugih rafinerijskih procesnih tokova, pa i koncentriranje vodika iz proizvedenog plina platforming procesa. Međutim, budući da vodik dobiven platforming procesom sadrži lagane ugljikovodike od 1 do 6 C od 25 do 35 vol.%, negativna posljedica ovakvog pročišćavanja vodika su gubici svih količina adsorbiranih ugljikovodika koji tijekom depresiranja (desorpcije) završavaju u sustavu loživog plina (Tail Gas). S tim količinama ugljikovodika se tada gubi i određeni dio vodika što ovisi o procesnim parametrima pod kojima radi sustav PSA.

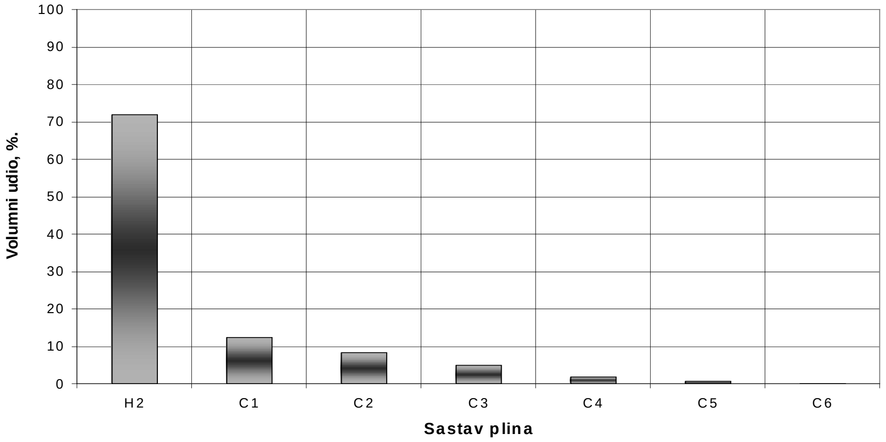
RNR planira izgradnju PSA sustava kako bi se osigurala visoka čistoća vodika potrebnog za hidrodesulfurizaciju plinskih ulja (za proizvodnju dizelskih goriva prema EU specifikacijama) i sirovine za katalitički kreking plinskih ulja .

Za razliku od tehnologije PSA sustava, jedan od najzanimljivijih aspekata pokretanja apsorpcijske kolone 17-C1 ostvaren je njezinim spajanjem s niskotlačnim sustavom postrojenja platforminga 2. Stabilizacijska kolona 12-C2 dobila je dodatnu funkciju stripiranja zasićenog apsorbensa. Time se pored obogaćivanja vodika dobilo i znatno povećanje iscrpka tekućeg plina na postrojenju platforming 2. To povećanje se ogleda u povećanju iscrpka ukapljenog naftnog plina standardne kvalitete i do 18% na vršnoj posudi stabilizacijske kolone 12-C2. Ovo povećanje iscrpka se postiglo i kasnijim dodatnim hlađenjem stabiliziranog reformata (apsorbensa), izvan postrojenja platforminga 2, a prije apsorpcijske kolone 17-C1.

Ukapljeni naftni plin, produkt platforming procesa ne zahtijeva dodatnu obradu i rafiniranje u svezi sadržaja sumpora. To je dodatna prednost u proizvodnji ukapljenog naftnog plina kao jednog od bitnijih rafinerijskih produkata. Do pokretanja kolone za kontinuiranu apsorpciju 17-C1 i njezinog spoja s platformingovom stabilizacijskom kolonom u rafinerijskom sustavu loživog plina se gubilo i do 17500 kg ukapljenog naftnog plina na dan.

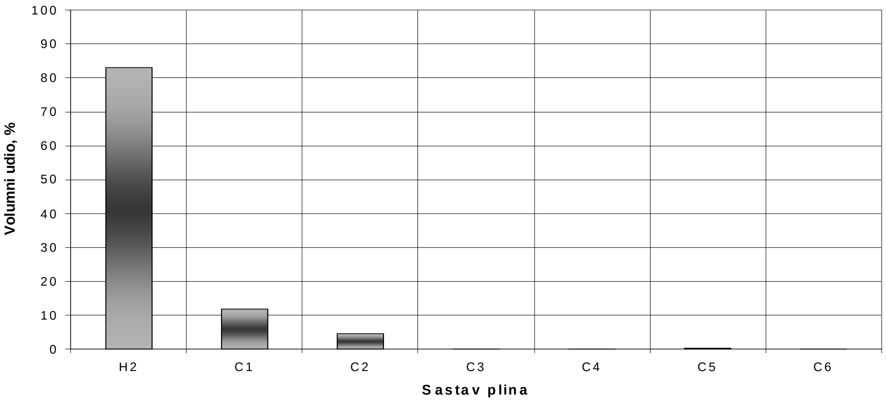
Pročišćavanje vodika fizikalnom apsorpcijom je zbog tehnoloških ograničenja opreme i procesnih fluida limitirano na maksimalno povećanje koncentracije vodika od 85 % vol, što zadovoljava trenutačne potrebe u RNR. Ipak, neovisno o procesnim parametrima kontinuirane fizikalne apsorpcije, za izlaznu čistoću vodika najvažniji je sadržaj metana u net separator plinu platforminga.

Slika 2: Sastav plina sa 12- V6 kroz cijeli ciklus platforminga 2
Figure 2: Composition of gas from 12- V6 throughout the Platforming 2 cycle



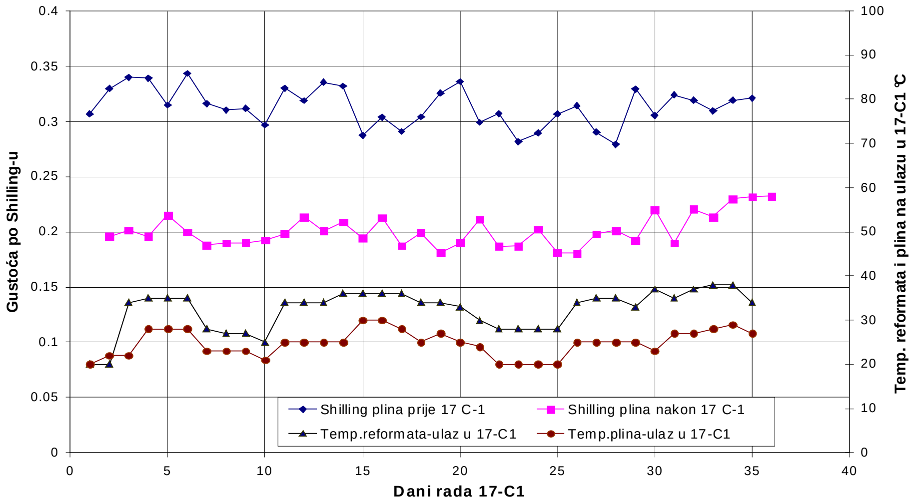
volumni udio=volume share, sastav plina=gas composition

Slika 3: Sastav plina na izlazu iz 17-C1
Figure 3: Gas composition at the exit from 17-C1



volumni udio=volume share, sastav plina=gas composition

Slika 4: Gustoća plina prije i poslije apsorbera te utjecaja temperature ulaznih struja na gustoću plina sa vrha 17-C1
Figure 4: Gas density before and after absorber and impact of the input currents' temperature on the density of gas from the top of 17-C1

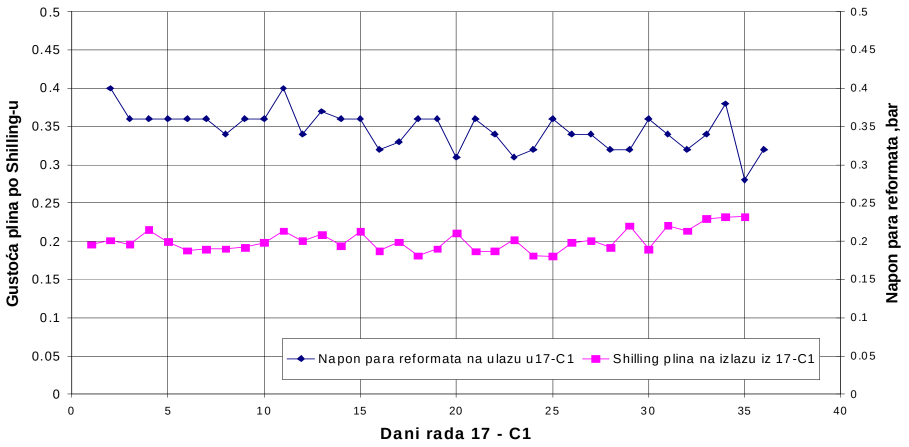


gustoća po Shillingu=Shilling density, dani rada=operating days, Shilling plina prije..=gas Shilling before., Shilling plina nakon...=gas Shilling after..,temperatura reformata i plina na ulazu u=reformate and gas temperature inlet...

Metan se zajedno s vodikom ponaša kao inertna komponenta procesa apsorpcije, i njegova veća koncentracija smanjuje čistoću vodika u plinu iza 17-C1. Ipak, rekuperiranje C3 i C4 ugljikovodika iz net separator plina platforminga 2 najveća je prednost rada apsorpcijske kolone 17-C1 nad PSA sustavima.

Integriranjem rada kolone 17-C1 s PSA sustavom, tj. obradom proizvedenog plina bogatog vodikom s platforminga 2 prije PSA, mogla bi se ostvariti oba efekta. Dakle, rekuperiranje vrednijih laganih ugljikovodika fizikalnom apsorpcijom pomoću kolone 17-C1, te uklanjanje preostalog metana iz izlaznog plina 17-C1 procesom adsorpcije u PSA, dobilo bi se znatno veće iskorištenje vodika, čistoće 99,99% vol. Uz to, odvojeni metan je idealna komponenta za proizvodnju vodika procesom steam reforminga a može se koristiti i kao loživi plin.

Slika 5: Ovisnost gustoće plina sa vrha apsorbera o naponu para ulaznog reformata
Figure 5: Dependence of the density of gas from the top of absorber on the vapour voltage of the input reformate



gustoća po Shillingu=Shilling density, dani rada=operating days, napon para reformata na ulazu...=reformate vapour pressure inlet.., Shilling plina na izlazu...=gas Shilling outlet...

RASPRAVA REZULTATA

U tablicama su prikazani rezultati rada apsorbera 17–C1 nakon njegova spajanja s postrojenjem platforminga 2 tijekom nešto više od mjesec dana. Može se vidjeti da apsorber povećava čistoću vodika u make–up plinu za HDS–BHK od 14 do 16%. Kromatografske analize ulaznog i izlaznog plina pokazuju da se vodik i metan ponašaju kao inertne komponente, jer je njihova koncentracija relativno veća u izlaznom plinu iz 17–C1. Volumni udio etana u izlaznom plinu apsorbera je za oko

44% niži od njegovog udjela na 12–V6 dok se više od 99% propana uklanja iz plina sa platforminga 2. Volumni udio izo i n-butana u izlaznom plinu je od 90 do 98% manji od njegovog udjela u plinu sa separatora 12–V6. Istovremeno je primiječen porast sadržaja tih ugljikovodika u reformatu s dna 17–C1 te znatno veće izdvajanje suhog plina u posudi 12–V7. Povećanjem tlaka u debutanizeru 12–C2 za 2 bara smanjuje se udio C_3 (s prosječnih 31 na oko 28%) i C_4 ugljikovodika u suhom plinu koji su prevedeni u tekući plin.

Budući da reformat s dna 12–C2 ne sadrži propan, posebno zanimljiv podatak o uspješnosti apsorpcije je volumni udio propana u izlaznom reformatu iz apsorbera koji raste čak do 2,4% vol. u zadnjoj analizi. Posljedica otapanja laganih ugljikovodika je relativno smanjenje sadržaja C_6+ ugljikovodika u reformatu na izlazu iz 17–C1 čija gustoća pada s istodobnim porastom napona para.

ZAKLJUČAK

Iz svih rezultata vidi se da apsorber vrši svoju funkciju, tj. da daje dovoljnu čistoću vodika za rad BHK–načina postrojenja HDS-BHK. To potvrđuje i sam rad postrojenja HDS–BHK koji sada kao šaržu uzima smjesu vakuum plinskih ulja uz gotovo 100% projektnog kapaciteta (60000 kg/h). Uz iscrpak laganog i teškog benzina te desulfuriziranog plinskog ulja ostatak s dna stripera se vodi kao šarža za FCC, pa je sadržaj sumpora u npr. benzinu FCC-a pao s 1000 do 1700 na oko 150 do 300 ppm. To je znatno olakšalo rafinaciju produkata postrojenja FCC (Merox UNP-a i Merox benzina). Istodobno je porastao iscrpak benzina, UNP-a i lakog katalitičkog ulja uz smanjenje iscrpka suhog plina. Najvažnija reakcija hidroobrade FCC-šarže je reakcija zasićenja polinuklearnih aromatskih spojeva čime se postiže veći prinos benzina. Uz smanjenje prinosa koksa na katalizatoru, hidroobradom se osim sadržaja sumpora u šarži FCC–a smanjuje i sadržaj teških metala te dušičnih spojeva. Metali su otrovi za katalizator FCC-a, jer zbog svoje dehidrogenacijske sposobnosti smanjuju katalitičku aktivnost uz proizvodnju vodika i također koksa na katalizatoru. Samim tim smanjuje se i vijek katalizatora (katalizator s previsokom količinom metala mora se zamijeniti). S druge strane, dušični aromatski spojevi su glavni otrov za kiselu funkciju katalizatora (obično prolaznog karaktera) čime se umanjuje sposobnost nastajanja karbonij-iona te cijepanje dugolančanih molekula u samom reaktoru. Iz svega ovoga može se zaključiti da rad postrojenja HDS–BHK u BHK načinu znatno doprinosi i optimiranju rada postrojenja fluid katalitičkog krekinga uz optimalniju proizvodnju bijelih produkata. Bez hidroobrađene FCC šarže nema uvjeta za proizvodnju niskosumpornog FCC benzina koji je jedna od glavnih komponenata za namješavanje motornih benzina. Proizvodnjom niskosumpornog FCC benzina udio te komponente u blendingu komercijalnih benzina (prvenstveno bezolovnih) povećava se s dosadašnjih 30–35% na 50–55%. Ovakav način blendinga komercijalnih benzina omogućava zadovoljavanje sve strožih zahtjeva na sadržaj ukupnih aromata, benzena i sumpora.

Apsorpcijska kolona 17–C1 se ne može i ne smije promatrati neovisno od procesnih parametara platforminga 2. Glavni razlog za aktiviranje kolone 17–C1 bila je prije svega težnja ka većoj čistoći vodika u RNR i optimalnom radu postrojenja HDS–BHK. Međutim, ono što je također jako bitno napomenuti jest to da se radom kolone 17–C1 znatno povećala produkcija ukapljenog naftnog plina s vrha kolone 12–C2 (12–V7). Vjerojatno tehnološki i ekonomski, najidealnijom spregom kolone 17–C1 sa stabilizacijskom kolonom platforminga 2, rad kolone 17–C1 se također može opisati i kao proces rekuperacije C_3+ ugljikovodika iz net–separator plina platforminga 2. Pročišćavanjem proizvedenog platformingovog plina s oko 72 na 83 % vol. svi u reformatu apsorbirani ugljikovodici rekuperiraju se na koloni 12–C2.

To je prednost rada kolone za kontinuiranu fizikalnu apsorpciju 17-C1 nad PSA sustavima ugrađenim na toku net separator plina katalitičkog reforminga.

Time se znatno povećava iscrpak ukapljenog naftnog plina na platformingu. Pored povoljnije ekonomske bilance, ovaj ukapljeni plin nije potrebno rafinirati što omogućava i veću slobodu u namješavanju UNP različitih specifikacija u Rafineriji nafte Rijeka.

Iz kromatografskih analiza ulaznog i izlaznog (”obogaćenog”) reformata iz kolone 17–C1 može se vidjeti da se radom kolone 17–C1, iscrpak ukapljenog plina na platformingu 2 povećava s prosječnih **8,36** na **9,42** m3/h.

Proizvodnja UNP-a ovisi o kvaliteti ulazne šarže, kao i oštrini rada platforminga, ali gledano na prosječni iscrpak nakon aktiviranja kolone 17–C1 to je povećanje iscrpka od **12,6** % vol. uz iste uvjete na stabilizacijskoj koloni 12–C2. Ovaj rezultat se odnosi na vremensko razdoblje od 30 dana nakon aktiviranja kolone 17–C1.

Naknadnim poboljšanjem procesa apsorpcije u koloni 17–C1 dodatnim hlađenjem debutaniziranog reformata, odnosno aktiviranjem vodenog hladnjaka 17–E11 na ulazu u 17–C1, količina rekuperiranog plina se prosječno povećala za **18** % vol. za isto vremensko razdoblje.

To je prosječno povećanje iscrpka UNP-a za **15,3** % vol. na postrojenju platforming 2. U odnosu na količinu proizvedenog ukapljenog naftnog plina na platformingu 2 za 2001. godinu od 39358 tona, može se zaključiti da je kolona 17–C1 povećala iscrpak UNP-a za **6025,9** tona/god (340 dana rada platforminga 2).

Ove količine su direktna posljedica procesnih parametara na platformingu 2 (RON=99, 75 m3/h unifinata, 17-24 bara u visokotlačnom separatoru). Eventualno većom produkcijom UNP-a na platformingu, sprega kolona 17–C1 i 12–C2 dala bi još veći doprinos povećanju iscrpka ukapljenog naftnog plina na postrojenju platforming 2.

INCREASING HYDROGEN PURITY BY ABSORPTION

Abstract

High environmental standards are nowadays being growingly adopted as requirements of the market and, subsequently, hydrotreating is gaining priority in oil processing. This, first of all, refers to sulphur content in fuels, which ultimately endangers the future existence of many refiners worldwide.

This was the main reason for constructing the new plant for HDS/MHC of heavier oil fractions at the Rijeka Refinery. Hydrogen quantities and its purity have become a very significant parameter in optimizing the Refinery's operation. The availability of sufficient hydrogen and its purity not only influence the level of process utilization but are also the key factor in meeting the highly severe requirements on sulphur content in oil products.

In Rijeka Refinery, like in many others, the Platformer unit is the only hydrogen producing unit. The purity of hydrogen ranges from 65 to 75% vol., depending on process parameters in the existing platformers. Since hydrogen purity proved to be quite a limiting factor for hydrotreating and hydrocracking processes, the ways of enriching platformer "net-separator gas" were sought for.

The Refinery experts are well acquainted with the processes for the production of pure hydrogen from light and heavy oil fractions and natural gas. However, construction of such process units would involve significant additional costs and time. The same applies to processes for purification of hydrogen-rich gases. These facts have triggered the search for the optimum solution leaning on the Refinery's own resources.

The results were not only the optimization of the Platformer unit but also the utilization of a part of the existing refinery's process equipment for the generation of higher purity hydrogen.

The conceptual design was developed and theoretical, technological and technical documents elaborated to support the realisation of the process for the production of higher purity hydrogen by means of absorption, which should take place on the 17 C-1 column. It should be mentioned that the 17 C-1 column is physically incorporated into the Tatoray process and has been out of service for some 12 years.

Thus, the 17 C-1 column becomes the absorber in the technical-technological sense, absorbing light hydrocarbons from

“net-separator gas” produced on Platformer 2. In our case, the absorbent is the stabilized and cooled down platformate showing high absorbing characteristics.

By connecting the 17-C1 column with the Platformer 2 stabilizer, the stabilizer has taken over the role of stripping the absorbed hydrocarbons from the absorbent (cooled platformate) which is separated as dry gas and LPG at the stabilizer overhead vessel.

The inclusion of the continuous absorbtion column into the Platformer 2 process has proved to have multiple favourable effects:

1. *The main target has been achieved: that of upgrading the Platformer 2 gas to contain over 83% vol. of hydrogen;*
2. *Through absorbtion of valuable hydrocarbons from the platformer gases (C_3 and C_4) the LPG yields at the Platformer unit have been significantly increased;*
3. *The gas purity with over 83% vol. of hydrogen content has enabled us to run the HDS/MHC plant in both modes at its maximum capacity and operating severity, yielding optimum quality products;*
4. *The plant run in HDS mode produces the maximum quantity and quality of gas oil, i.e. of diesel fuel;*
5. *MHC mode generates the maximum quantity and the required quality of the FCC feed. By processing the properly hydrotreated feed, additional favourable effects are achieved. These are, first of all, increased yields of gasoline, LPG and LCO at the expense of less valuable decanted oil and dry gas. All FCC products show the minimum sulphur level which ultimately has a favourable influence on the blending of commercial products.*

INTRODUCTION

Environmental requirements are today increasingly becoming also the requirements of the market, which was the main reason for investing into and constructing a new HDS plant for heavier oil fractions at the Rijeka Oil Refinery. In 1997, a new plant for hydrodesulphurization and mild hydrocracking (HDS–MHC) has been launched, manufactured by the IFP company (Institut Francais du Petrole). Due to the need for a wider range of the input charge with regard to both specific density and the volume of undesirable compounds in the feed itself (primarily unsaturated compounds, sulphur and aromatic nitrogen compounds, and heavy metal compounds), the plant has been designed for two modes of operation: HDS and MHC. The desire was to achieve the HDS–MHC plant’s flexibility, and its lesser sensitivity to major oscillations in feed quality at the Rijeka Oil Refinery.

The HDS operating mode is envisaged for the hydrodesulphurization of the compound of light gas oil from the atmospheric oil distillation and light catalytic oil (an FCC product), thus ensuring the production of the main component for the blending of commercial diesel fuels.

The MHC operating mode has been designed for the hydrotreatment of the feed consisting of the vacuum heavy and vacuum light gas oil, with the products being hydrotreated gasoline and hydrotreated gas oil and the residue, being the feed for the Fluid Catalytic Cracking plant. This plant’s operating mode considerably optimizes the production of white products at the Rijeka Oil Refinery, as well as the operation of the Fluid Catalytic Cracking plant itself (easier cracking reactions at the reactor itself), whose products contain considerably lower sulphur volumes.

Already in the first operating cycle of the HDS–MHC plant, an imperfection in hydrogen purity was established in its recirculating gas. Although, before launching the HDS-MHC plant, the catalyst was replaced at the Platforming 2 plant, for the purpose of obtaining higer volumes of higher purity hydrogen, the expected results have not been achieved. The purchase of new platforming catalysts was supposed to enable higher volumes of generated gas (make-up for HDS–MHC), enabling minimal hydrogen purity in the circulating gas of the HDS–MHC plant in the amount of 73%.

However, due to the severe operating regime of the Platforming proces, the quality of processed charge, and gradual catalyst deactivation, the hydrogen purity did not meet the needs of project and process conditions at the HDS-MHC plant. It should be pointed out that the volumes of gas from the Platforming 2 plant were sufficient, but still the main limitation was the purity of hydrogen in the recirculating gas of the HDS-MHC plant. Due to all of the above reasons, the processing capacity of the HDS-MHC plant was limited in both modes. Such a situation was absolutely not acceptable in the optimization process of the Rijeka Oil Refinery’s operation.

Since the Platforming process is the only hydrogen producer at the Rijeka Oil Refinery, all the activities were directed towards finding an acceptable solution for increasing the produced hydrogen’s purity.

Connecting the Absorption Column with Platforming 2

Refinery experts have long been acquainted with the processes of producing pure hydrogen from both lighter and heavier oil or natural gas fractions. However, the construction of such processes requires considerable additional investments and time. The same goes for the construction of the well-known technological processes for the purification of hydrogen-rich gases. The said facts have made us urgently find an optimal solution within the Refinery.

The solution was found in launching a part of the section for hydrogen enrichment Tatoray, the column for continuous absorption 17-C1.

The first purpose of the Tatoray plant was the hydrodealkylation of C7 aromatics, and, by 1990, it was operating under the name Hydeal. Hydeal had a section for enriching its circulating gas by hydrogen consisting of column 17–C1 together with the stripper column 17–C2 which was used for the stripping of absorbed hydrocarbons from the absorbent (toluene). With the change of the Hydeal's purpose into Tatoray, the 17–C1 column was no longer operative as an absorber, because in the aromatics transalkylation process, the consumption of hydrogen is neglectable, so that the make–up from Platforming 2 was sufficient.

Due to the lack of certain equipment parts on the absorbent stripper, and particularly due to the lack of thermal energy for the stripping of saturated absorbent, the 17–C1 column was connected to the low pressure system of Platforming 2. As absorbent, we have used the cooled and stabilized reformate (not containing C_4-), while the Platforming 2 stabilization column took over the role of stripping absorbed hydrocarbons from the absorbent.

Thus, apart from increasing hydrogen purity in the make-up gas for the HDS-MHC plant, we have obtained also increased LPG use on Platforming 2, through its increased isolation on the stabilization column top vessel.

Depending on process parameters in the existing ROR Platforming processes, hydrogen purity ranges from 65 to 75% vol. By putting on stream the absorber column of the Tatoray process on the flow of the make-up gas at the HDS-MHC plant, hydrogen concentration increase of up to over 83% vol. may be achieved. Such effects are achieved with the volume flow of up to as much as 12,000 Nm^3/h of gas through the absorption column 17-C1, which is 20 % higher than its designed capacity.

It should be mentioned that, without an optimal operation of Platforming 2, the absorption of light hydrocarbons into platformate at the 17–C1 column would not be efficient in achieving sufficiently high partial hydrogen pressure in the make–up gas for HDS-MHC. This refers to the inevitable Platforming 2 severity of operation, and project capacities of its low pressure system (load of the stabilization column and of the furnace for its reboiling). Optimal operation of Platforming 2, apart from the octane number and the volume of reformates, as well as the liquid gas volume, takes also the gas produced at the high pressure separator as a very important process product.

Recuperation of C3 and C4 hydrocarbons

The standard UOP semi-regenerative Platforming process does not envisage the enrichment of its produced gas. The so far widely known solution for the concentration of hydrogen which is in compound with other gases are the PSA systems (Pressure Swing Adsorption). PSA systems are usually used as an additional part of the equipment after the main hydrogen production process (Steam reforming) and are operating on the principle of gas adsorption and a solid adsorbent. Unlike other gases, hydrogen is – due to its properties - not adsorbed under process conditions of the PSA system, so that through the PSA process hydrogen purity in the output gas is increased to 99.99% vol. PSA systems may – due to their resistance to aggresive gases - apart from the Steam reforming operation finalization – also be used for hydrogen concentration from other refinery process flows, even for hydrogen concentration from the gas produced at the Platforming process. However, since hydrogen obtained through Platforming process contains light hydrocarbons of 1 to 6 C from 25 to 35 vol.%, the negative consequence of such hydrogen purification are the losses of all adsorbed hydrocarbon volumes which during depressing (desorption) end up in the Tail Gas system. Along with these hydrocarbon volumes, also lost is a certain part of hydrogen, depending on process parameters under which the PSA system is operating.

The ROR is planning the construction of PSA system in order to ensure high purity of hydrogen necessary for the hydrodesulphurization of gas oils (for the production of diesel fuel according to EU specifications) and feeds for the catalytic cracking of gas oils .

Unlike the PSA system technology, one among the most interesting aspects of launching the absorption column 17-C1 has been realized through its connection to the low pressure system of the Platforming 2 plant. Stabilization column 12-C2 has gained the additional function of stripping the saturated absorbent. Apart from hydrogen enrichment, this has also resulted in increased fluid gas yield at the Platforming 2 plant. This increase has in turn resulted in increased LPG yield (of standard quality) up to 18 % at the 12-C2 stabilization column overhead vessel. This yield increase has also been achieved by a later additional cooling of the stabilized reformate (absorbent), outside the Platforming 2 plant, and before the 17-C1 absorption column.

LPG, the Platforming process product, does not require additional treatment or refining with regard to sulphur content. This constitutes an additional advantage in the production of Liquid Petroleum Gas, as one among more significant refinery products. Before the launching of the 17-C1 continuous absorption column and its connection to the Platforming’s stabilization column, the refinery fuel gas system was loosing up to 17,500 kg of LPG per day.

Hydrogen purification using physical absorption is due to technological limitations of equipment and process fluids limited to the maximal hydrogen concentration increase of 85% vol., meeting the Refinery’s current needs. Still, regardless of the process parameters of continuous physical absorption, for the output hydrogen purity, the most important is methane content in the net separator gas of the Platforming.

Methane, together with hydrogen, behaves as an inert component of the absorption process, and its highest concentration reduces hydrogen purity in the gas after 17-C1. Still, the recuperation of C3 and C4 hydrocarbons from the net separator gas of Platforming 2 is the greatest advantage of the absorption column 17-C1 operation over PSA systems.

By integrating the operation of the 17-C1 column with the PSA system, i.e. the treatment of hydrogen-rich gas produced at Platforming 2 before PSA, it would be possible to achieve both these effects. Therefore, the recuperation of more valuable light hydrocarbons through physical absorption using column 17-C1, and removal of residual methane from the output gas of 17-C1 through the adsorption process in PSA, would obtain a much higher utilization of hydrogen with the purity of 99.99% vol. Also, the separated methane is an ideal component for hydrogen production using the Steam reforming process, while it may also be used as fuel gas.

DISCUSSION OF RESULTS

The Tables show the results of operation of absorber 17–C1 after its connection to the Platforming 2 plant over somewhat more than a month. One may observe that the absorber increases hydrogen purity in the make–up gas for HDS–MHC from 14 to 16%. Chromatographic analyses of the input and output gas show that hydrogen and methane act as inert components, because their concentration is relatively higher in the output gas from 17–C1. The ethane volume share in the output gas from the absorber is about 44% lower than its share in 12–V6, while over 99% pf propane is removed from the gas from Platforming 2. The volumetric share of iso and n-butane in the output gas is from 90 to 98% lower than its share in the gas from the 12–V6 separator. At the same time we have observed an increase in the content of the same hydrocarbons in the reformate from the bottom of 17–C1, and a much higher isolation of dry gas in the 12–V7 vessel. By increasing pressure in debutanizer 12–C2 for 2 bar, the dry gas share of C_3 (from the average 31 to around 28%) and C_4 hydrocarbons, transformed into liquid gas, is reduced.

Since the reformate from the bottom of 12–C2 does not contain propane, especially interesting datum on the success of the absorption is the volume share of propane in the output reformate from the absorber increased up to 2.4% vol. in the last analysis. The consequence of light hydrocarbons dissolution is the relativne lowering of the C_6+hydrocarbons content in the reformate at the exit from 17–C1, whose density decreases with the simultaneous vapour pressure increase.

CONCLUSION

It may be seen from all of the above results that the absorber is fulfilling its function i.e. that it provides sufficient hydrogen purity for the operation of MHC–mode of the HDS-MHC plant. This is confirmed by the very operation of the HDS–MHC plant which is now taking as charge a compound of vacuum gas oils with nearly 100% of the project capacity (60,000 kg/h). With the yield of light and heavy gasoline and desulfurized gas oil, the residue from the bottom of the stripper is conducted as charge for FCC, which is why sulfur content in FCC gasoline for instance is reduced from 1000-1700 to around 150-300 ppm. This has considerably facilitated the refinement of the FCC plant products (Merox LPG and Merox gasoline). At the same time, the yield of gasoline, LPG, and light catalytic oil went up, with the reduction of dry gas yield. The most important FCC-feed hydrotreatment reaction is that of polynuclear aromatic compounds saturation, obtaining higher gasoline yield. With reduced coke yield at the catalyst, the hydrotreatment – apart from the FCC–feed sulphur content – reduces also the heavy metals content, as well as that of nitrogen compounds. Metals are poisons for the FCC catalyst, because, due to their dehydrogenation ability, they reduce catalytic activity, with hydrogen and also coke production on the catalyst. This reduces the catalyst's service life (catalyst with too high metal content must be replaced). On the other hand, nitrogen aromatic compounds are the main poison for the catalyst's acid function (usually of transitory character), thus reducing the ability to generate carbonium–ions and splitting of long-chained molecules at the very reactor. All this points to the conclusion that the operation of HDS–MHC plant in MHC mode has a considerable contribution to the operation optimization of the Fluid Catalytic Cracking plant with a more optimal production of white products. Without hydrotreated FCC charge, there are no conditions for producing low sulphur FCC gasoline, being one among the main components for the blending of motor gasoline. Through the production of low sulphur FCC gasoline, the share of this component in the blending of commercial gasoline (primarily those unleaded) increases from the present 30–35% to 50–55%. Such a manner of blending commercial gasoline enables the meeting of increasingly stringent requirements imposed upon the content of total aromatics, benzene and sulphur.

The absorption column 17–C1 cannot and should not be observed independently from the process parameters of Platforming 2. The main reason for activating column 17–C1 was primarily the desire to achieve higher hydrogen purity at ROR and optimal operation of the HDS–MHC plant. However, it is also very important to point out that the operation of the 17–C1 column has considerably increased the production of LPG from the top of the column 12–C2 (12–V7). In technological and economic terms probably the most ideal connection of the 17–C1 column with the stabilization column of Platforming 2, the operation of the 17–C1 column may also be described as the recuperation process of C_3+ hydrocarbons from the net–separator gas of Platforming 2. Through the purification of the produced Platforming gas from around 72 to 83 % vol., all the hydrocarbons absorbed in the reformate are recuperated at the 12–C2 column.

This is the operating advantage of the column for continuous physical absorption 17-C1 over the PSA systems installed on the flow of the Catalytic Reforming net separator gas.

This considerably increases the yield of LPG at Platforming. Apart from a more favourable economic balance, this LPG need not be refined, enabling a larger freedom in the blending of various specification LPGs at the Rijeka Oil Refinery.

Chromatographic analyses of input and output (”enriched”) reformate from column 17–C1 show that, through the operation of the 17–C1 column, the LPG yield at Platforming 2 goes up from the average **8.36** to **9.42** m^3/h.

LPG production depends on the quality of the input charge, as well as Platforming's severity of operation, but, given the average yield after activating column 17–C1, it is a yield increase of **12.6** % vol. under the same conditions at the stabilization column 12–C2. This result refers to the time period of 30 days after the activation of the 17–C1 column.

Through subsequent improvement of the absorption process in column 17–C1 through additional cooling of debutanized reformate, i.e. activation of the water cooler 17–E11 at the exit into 17–C1, the volume of recuperated gas has increased for **18** % vol. on the average for the same time period.

This constitutes an average LPG yield increase by **15.3** % vol. at the Platforming 2 plant. With regard to the volume of LPG produced at Platforming 2 in 2001 in the amount of 39,358 tons, we may conclude that the 17–C1 column has increased LPG yield by **6025.9** tons/year (340 days of Platforming 2 operation).

These volumes are a direct consequence of process parameters at Platforming 2 (RON=99, 75 m^3/h unifinate, 17-24 bar at the high pressure separator). Through a possibly higher LPG production at the Platforming, the connection between 17–C1 and 12–C2 columns would provide an even greater contribution to the increase of LPG yield at the Platforming 2 plant.

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665.644.442-403 frakcija plinova platforminga	platformate gas
665.644.442 : 661.96 vodik platforminga za HDS/BHC	platformate hydrogen for HDS/MHC
665.644.442.071.7 apsorpciona kolona platformera	absorption tower of platformer plant
661.96.071.7 pročišćavanje vodika absorpcijom	hydrogen purification by absorption
665.658.26 hidrodesulfurizacija /blagi hidrokreking HDS/BHK	hydrodesulphuration /mild hydrocracking HDS/MHC
665.6 : 061 INA RnR INA Industrija nafte Rafinerija nafte Rijeka	INA Oil industry Rijeka Refinery

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