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POBOLJŠANJE KVALITETE MOTORNIH BENZINA SMANJENJEM SADRŽAJA SUMPORA U FCC BENZINU

Sažetak

Benzin dobiven procesom fluid katalitičkog krekinga jedan je od najvećih izvora sumpora u proizvodnji motornih benzina Rafinerije nafte Rijeka. Trenutačno primjenjivi standardi dopuštaju maksimalni sadržaj sumpora od 150 ppm, dok će u 2005. godini biti primjenjiv standard s dopuštenih maksimalnih 50 ppm sumpora u motornim benzinima. Budući da se izgradnja postrojenja koje rješava problem sumpora u rafineriji ne očekuje prije 2006. grupa stručnjaka Rafinerije nafte Rijeka predložila je prijelazno rješenje korištenjem postojećih postrojenja rafinerije u svrhu frakcionacije i uklanjanja sumpora u FCC benzinu.

U tu svrhu postavljeni su matematički modeli sekcije postrojenja atmosferske destilacije, te postrojenja Unifining i HDS. Istraživani su i proučeni optimalni radni uvjeti procesa simuliranjem, te je predloženo optimalno rješenje s obzirom na raspoloživu procesnu opremu, zahtijevane kapacitete, zahtijevano smanjenje količine sumpora uz kriterij minimalnog gubitka oktanskog broja benzina kao i raspoložive količine energenata.

1.0. Uvod

Sve stroži zahtjevi zaštite okoliša utječu na proizvođače motornih goriva da poboljšavaju svojstva svojih proizvoda, između ostalog i smanjenjem udjela sumpora u motornim benzinima. Najveći doprinos sumpora u benzinima dolazi od FCC benzina, koking benzina i teškog benzina iz procesa atmosferske destilacije, a pritom je najveći izvor sumpora upravo FCC benzin koji doprinosi čak 40-90 % sumpora u motornom benzinu[5]. Smanjenje udjela sumpora u FCC benzinu se provodi:

(1) Hidroobradom sirovine FCC-a,

(2) Hidroobradom FCC benzina.

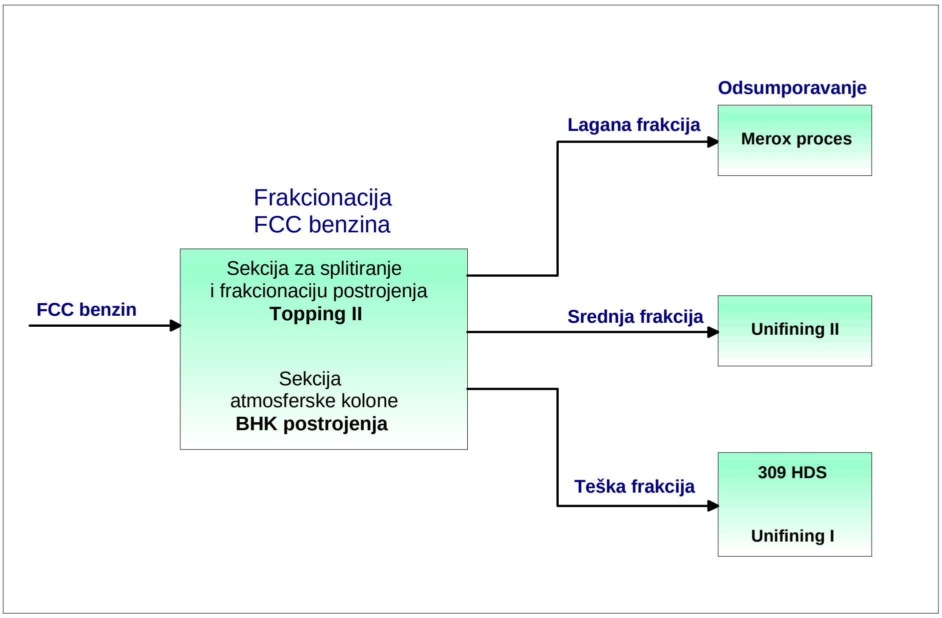
Hidroobrada cjelokupne frakcije FCC benzina rezultira značajnim smanjenjem udjela sumpora, ali također kao posljedicu ima i znatno smanjenje oktanskog broja zbog zasićenja olefina. Poznata je činjenica da je udio olefina veći u lakšim frakcijama, dok udio sumpora raste u težim frakcijama, stoga je logično rješenje frakcionacija FCC benzina, te zatim hidroobrada teške frakcije, što rezultira minimalnim gubitkom oktanskog broja.[1]

Tablica 1: Svojstva motornih benzina prema europskim standardima

	Maksimalna dopuštena koncentracija sumpora, ppm	
	Motorni benzini	Dizelska goriva
Europski standard	EN-228	EN-590
1.1.2000.	150	350
1.1.2005.	50	50
1.1.2009.	10	10

Rafinerija nafte Rijeka ima ograničene mogućnosti hidroobrade FCC sirovine na postrojenju HDS/BHK (hidrodesulfurizacija i blagi hidrokreking) zbog potrebe za velikom količinom dizelskih goriva niskog sadržaja sumpora zbog čega postrojenje uglavnom radi kao HDS.

Slika 1: Shema mogućih rješenja frakcionacije i odsumporavanja FCC benzina



Izgradnja novih postrojenja koja će omogućiti dugoročno rješenje kvalitete goriva s ultra niskim sadržajem sumpora se tek očekuje. Nužna je što brža prilagodba europskim standardima kvalitete goriva, jer od 1.1.2005. počinje primjena europskog standarda EN-228 s maksimalnim dopuštenim udjelom sumpora u motornim benzinima od 50 ppm, tablica 1. Grupa stručnjaka Rafinerije nafte Rijeka predložila je ideju frakcionacije FCC benzina na uglavnom slobodnim postrojenjima, te zatim hidroobrade dobivenih frakcija, kako je prikazano slikom 1.

2.0. Eksperimentalni dio

Sirovina: FCC benzin dobiven preradom nafte tipa REB, sastava prikazanog tablicom 2.

FCC benzin	REB
Gustoća, g/cm^3	0.735
Destilacija	
Početak, °C	26.7
5 % v/v, °C	33.9
10 % v/v, °C	37.2
20 % v/v, °C	44.0
30 % v/v, °C	51.7
40 % v/v, °C	62.6
50 % v/v, °C	98.3
60 % v/v, °C	103.7
70 % v/v, °C	146.3
80 % v/v, °C	158.1
90 % v/v, °C	172.0
95 % v/v, °C	182.7
Kraj °C, %v/v	209.4-98
Strukturni sastav (FIA)	
Aromati, %v/v	20.96
Olefini, %v/v	39.56
Parafini + nafteni, %v/v	38.88
Količina dušika, mg/kg	39.21
Bromni broj, mg/kg	60.41
Količina ukupnog sumpora, %m/m	0.11
Oktanski broj, istraživački IOB	90.6
Oktanski broj, motorni MOB	78.5

S ciljem istraživanja mogućnosti frakcionacije FCC benzina, te odsumporavanja i obrade proizvoda frakcionacije vodikom na postojećim postrojenjima Rafinerije nafte Rijeka provedena je analiza sljedećih procesa[2]:

(1) Procesi analizirani u svrhu frakcionacije FCC benzina:

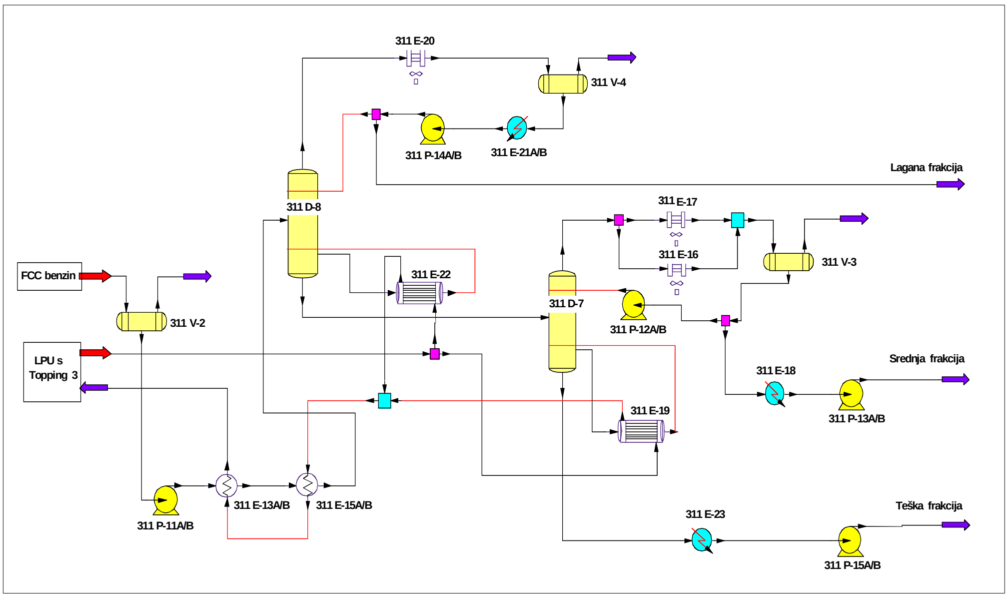
- sekcija za splitiranje i stabilizaciju postrojenja Topping II,
- sekcija atmosferske kolone BHK postrojenja.

(2) Procesi analizirani u svrhu hidroobrade teške frakcije FCC benzina:

- postrojenje 309HDS,
- postrojenje Unifining I.

Analiza procesa je provedena izradom simulacijskih modela na osnovi eksperimentalnih podataka s industrijskih procesa. Matematičkim simulacijskim modelima obuhvaćeni su reaktori, destilacijske kolone, separatori, izmjenjivači topline, crpke i kompresori. Pri izradi simulacijskih modela primjenjivan je programski sustav ChemCad 5.4[3], a simulacijski modeli postrojenja Topping II i BHK prikazani su slikama 2 i 3.

Slika 2: Simulacijski model sekcije za splitiranje i stabilizaciju postrojenja Topping II



Analiza je provedena za dva tipa nafte: REB i Sirian Light, te za različite protoke sirovine od 50 i 80 m^3/h i to za dva slučaja frakcionacije:

Slučaj 1

- lagana frakcija, vrelište <84 °C,
- srednja frakcija, vrelište 84-132 °C,
- teška frakcija, vrelište >132 °C.

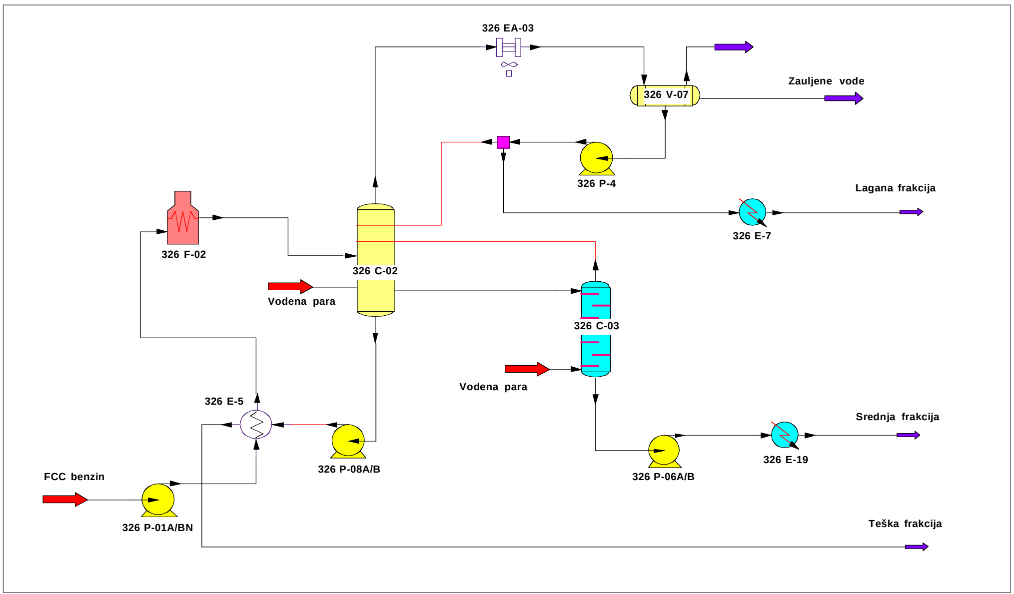
Slučaj 2

- lagana frakcija, vrelište <84 °C,
- srednja frakcija, vrelište 84-165 °C,
- teška frakcija, vrelište >165 °C,

Kao kriteriji za odabir optimalnog rješenja primijenjeni su:

- maksimalno smanjenje sadržaja sumpora,
- minimalno smanjenje oktanskog broja,
- maksimalna primjena raspoložive postojeće procesne opreme.

Slika 3: Simulacijski model sekcije atmosferske kolone BHK postrojenja



3.0. Rezultati i rasprava

3.1. Mogućnosti primjene postojećih postrojenja za frakcionaciju FCC benzina

Mogućnosti frakcionacije analizirane su na procesima BHK i Topping II. Provedenom je analizom zaključeno da postojeće postrojenje BHK nije primjenjivo za frakcionaciju FCC benzina bez zamjene kolona 326C-02 i 326C-03 kolonama s većim promjerom i većim brojem plitica.

Sekcija za splitiranje i stabilizaciju postrojenja Topping II primjenjiva je za frakcionaciju FCC benzina na proizvode za oba slučaja sječenja[2]; slučaj 1: laganu frakciju, vrelišta <84 °C, srednju frakciju, vrelišta 84-132 °C, i tešku frakciju, vrelišta >132 °C, i slučaj 2: laganu frakciju, vrelišta <84 °C, srednju frakciju, vrelišta 84-165 °C, i tešku frakciju, vrelišta >165 °C. Sekcija za splitiranje i stabilizaciju postrojenja Topping II omogućava i frakcionaciju između navedenih rezova. Za učinkovitu frakcionaciju nužne su prilagodbe postrojenja primjenom učinkovitijeg predgrijavanja pojenja kolone 311D-8.

3.2. Mogućnosti primjene postojećih postrojenja za odsumporavanje frakcija FCC benzina

U svrhu hidroobrade i odsumporavanja teške frakcije FCC benzina, vrelišta >132 °C proučavane su mogućnosti primjene postrojenja HDS i Unifining I. Teška frakcija FCC benzina, vrelišta >132 °C sadrži cca. 13 %v/v olefina, pa je primjena postrojenja 309HDS jedino moguće rješenje, zbog izvedbe reaktora u koji se uvodi plin za hlađenje (quench gas). Postrojenje Unifining I nema takvu izvedbu reaktora, pa u reaktoru zasićenjem olefina nastaje prevelik gradijent temperature. Zbog toga se hidroobrada teške frakcije, vrelišta >132 °C, a koji sadrži cca. 13 %v/v olefina na postojećem postrojenju Unifining I ne preporuča.

Srednju frakciju, vrelišta 84-132 °C, u količini od 13 m^3/h, moguće je miješati s benzinom dobivenim procesom Atmosferske destilacije i desulfurizirati na postrojenju Unifining II. Dodatnom se količinom od 13 m^3/h ne prelazi dozvoljeni bromni broj. Daljnom preradom na postrojenju katalitičkog reforminga poveća se oktanski broj benzina uz proizvodnju prijeko potrebnog vodika.

Lagana se frakcija odvodi na uklanjanje merkaptana u postrojenje Merox, ili bez dodatne obrade u mješalište (blending) benzina.

Mogućnost primjene postojećeg postrojenja Unifining I za obradu teške frakcije analizirana je uz pretpostavku obrade frakcije teškog benzina, vrelišta >155 °C. Frakcija teškog benzina vrelišta >155 °C sadrži cca. 10 %v/v olefina. Smanjena količina olefina smanjuje gradijent temperature u reaktoru i omogućava obradu tako proizvedene frakcije na postojećem Unifining I postrojenju.

3.3. Optimalno rješenje frakcionacije FCC benzina

Optimalno rješenje frakcionacije FCC benzina temelji se na:

- iskorištenju postojeće opreme,
- prilagodbi frakcionacije i sintezi topologije postrojenja sa svrhom maksimizacije iskorištenja kapaciteta raspoložive postojeće procesne opreme,
- maksimizaciji iskorištenja raspoložive toplinske energije.

Najveći nedostatak primjene sekcije za splitiranje i stabilizaciju Topping II u svrhu frakcionacije je nemogućnost grijanja medija pomoću peći. Analizom procesa pomoću simulacijskog modela predložen je optimalni raspored izmjenjivača topline u svrhu maksimalnog iskorištenja topline. Kao ogrjevni medij koristi se lako plinsko ulje koje se provodi s postrojenja Topping III. Ograničena količina LPU uvjetuje maksimalni kapacitet frakcionacije od 65 m^3/h, kako je prikazano tablicom 3.

Tablicom 3 i 4 prikazane su količine i svojstva proizvoda dobivenih frakcionacijom primjenom postrojenja Topping II.

Tablica 3: Kemijski sastav i svojstva frakcija FCC benzina, za frakcionaciju slučaj 1

Procesni tok	FCC benzin	Lagana frakcija <84 °C	Srednja frakcija 84-132 °C	Teška frakcija >132 °C
Protok, kg/h	47747.4	21020.3	9579.1	17148.0
Protok, m³/h (T i P)	65.8	32.6	13.3	20.6
Gustoća, g/cm³	0.735	0.662	0.750	0.837
Destilacija				
Početak, °C	26.7	25.6	95.3	145.8
5 % v/v, °C	33.9	32.0	98.2	151.5
10 % v/v, °C	37.2	33.8	98.6	151.9
20 % v/v, °C	44.0	36.9	99.6	154.0
30 % v/v, °C	51.7	39.9	100.7	157.1
40 % v/v, °C	62.6	43.2	101.4	159.8
50 % v/v, °C	98.3	46.7	102.2	163.0
60 % v/v, °C	103.7	50.4	104.2	168.5
70 % v/v, °C	146.3	54.6	106.3	173.6
80 % v/v, °C	158.1	59.9	108.7	180.0
90 % v/v, °C	172.0	66.6	113.4	188.9
95 % v/v, °C	182.7	71.4	117.9	196.5
Kraj °C, %v/v	209.4-98	75.8-98	125.1-98	209.4-98
Strukturni sastav (FIA)				
Aromati, %v/v	20.96	0.00	12.72	59.92
Olefini, %v/v	39.56	57.89	36.46	13.12
Parafini + nafteni, %v/v	38.88	42.11	50.82	26.96
Količina dušika, mg/kg	39.21	8.76	4.93	112.30
Bromni broj, mg/kg	60.41	85.80	62.68	18.92
Količina ukupnog sumpora, %m/m	0.11	0.03	0.12	0.23
Oktanski broj, istraživački IOB	90.6	-	87.5	92.8
Oktanski broj, motorni MOB	78.5	-	75.0	81.0

Tablica 4: Kemijski sastav i svojstva frakcija FCC benzina, za frakcionaciju slučaj 2

Procesni tok	FCC benzin	Lagana frakcija <84 °C	Srednja frakcija 84-165 °C	Teška frakcija >165 °C
Protok, kg/h	47747.4	20708.0	18588.1	8451.3
Protok, m^3/h	65.8	31.7	24.2	9.9
Gustoća, g/cm^3	0.735	0.662	0.777	0.861
Destilacija				
Početak, °C	26.7	25.9	101.8	174.9
5 % v/v, °C	33.9	31.2	107.9	177.5
10 % v/v, °C	37.2	33.1	110.2	178.1
20 % v/v, °C	44.0	36.3	113.1	179.0
30 % v/v, °C	51.7	39.7	115.1	180.2
40 % v/v, °C	62.6	43.2	117.5	181.2
50 % v/v, °C	98.3	46.9	121.1	182.5
60 % v/v, °C	103.7	51.0	125.9	184.1
70 % v/v, °C	146.3	55.6	131.5	186.6
80 % v/v, °C	158.1	61.2	137.8	190.5
90 % v/v, °C	172.0	68.2	145.0	196.8
95 % v/v, °C	182.7	73.7	150.2	202.5
Kraj °C, %v/v	209.4-98	78.7-97	156.1-98	217.4-98.5
Strukturni sastav (FIA)				
Aromati, %v/v	20.96	0.00	29.00	71.84
Olefini, %v/v	39.56	60.20	27.48	7.89
Parafini + nafteni, %v/v	38.88	39.80	43.52	20.27
Količina dušika, mg/kg	39.21	7.80	17.93	186.00
Bromni broj, mg/kg	60.41	85.33	43.98	13.80
Količina ukupnog sumpora, %m/m	0.11	0.04	0.16	0.26
Oktanski broj, istraživački IOB	90.6	-	88.0	93.7
Oktanski broj, motorni MOB	78.5	-	75.6	82.3

3.4. Opis procesa optimalnog rješenja frakcionacije

Sirovina, FCC benzin, dovodi se iz spremnika u prihvatnu posudu sirovine 311 V-2. Razina kapljevine u posudi regulira se pomoću regulatora razine LC-3 kaskadno povezanog s regulatorom protoka FC-3, koji regulira protok FCC-benzina u proces frakcionacije. Zaostala procesna voda odvaja se u odvajaču vode posude 311V-2. Razina vode regulira se pomoću regulacije razine LDC-2.

Pomoću crpke 311 P-11A/B, FCC benzin se provodi kroz izmjenjivače topline 311E-13 i 311E-15, u kojima se sirovina predgrijava lakim plinskim uljem, te zagrijana na 138 °C uvodi na 21 i 23 pliticu kolone 311D-8. U koloni 311D-8 odvaja se lagani FCC benzin od težih frakcija. U vrhu kolone 311D-8 izdvajaju se vršne pare koje kondenziraju u zračnom kondenzatoru 311E-20, i kao kapljevina odvode se u prihvatnu posudu pretoka ili refluksa 311V-4. Iz posude se ukapljeni ugljikovodici dodatno hlade kroz zračni hladnjak 311E-21, te zatim pomoću crpke 311P-14A/B dijelom vraćaju u kolonu kao refluks, dok se preostala količina ukapljenih ugljikovodika kao lagana frakcija FCC benzina odvodi u spremnik ili u daljnju obradu.

Tlak u posudi 311 V-4 regulira se pomoću regulatora tlaka PC-3B, a razina pomoću regulatora razine LC-6, koji djeluje na protok proizvoda lagane frakcije FCC benzina. Protok refluksa u striper regulira se pomoću regulatora protoka FC-10.

Ukapljeni ugljikovodici iz dna kolone 311 D-8 se dijelom isparuju u isparivaču 311E-22 pomoću lakog plinskog ulja, čiji se protok regulira s FC-13. Ispareni ugljikovodici uvode se u dno kolone, dok se proizvod dna stripera odvodi u kolonu 311 D-7.

Razina u koloni 311 D-8 regulira se pomoću regulatora razine LC-4, koji djeluje na protok proizvoda dna kolone, dok se tlak regulira pomoću regulatora tlaka PC-3A, koji djeluje na protok vršnih para u prihvatnu posudu pretoka.

Iz vrha kolone 311D-7 odvode se vršne pare kroz paralelno povezane zračne kondenzatore 311E-16 i 311E-17, a zatim se kao kapljevina sakupljaju u prihvatnoj posudi pretoka ili refluksa 311V-3.

Tlak u posudi 311V-3 regulira se pomoću regulatora tlaka PC-2B.

Ukapljeni ugljikovodici iz posude 311V-3 dijelom se pomoću crpke 311 P-12 vraćaju u kolonu kao pretok, dok se drugi dio, srednja frakcija FCC benzina, pomoću crpke 311P-13 provodi kroz hladnjak 311E-18 i odvodi u spremnik. Razina u prihvatnoj posudi refluksa regulira se pomoću regulatora razine LC-5, koji djeluje na protok proizvoda srednje frakcije FCC benzina.

U dnu kolone 311D-7 izdvajaju se ukapljeni ugljikovodici, koji dijelom isparuju u isparivaču 311E-19, zagrijavanjem pomoću lakog plinskog ulja. Protok LPU se regulira pomoću regulatora protoka FC-12. Ispareni ugljikovodici vraćaju se u dno kolone 311 D-7.

LPU se iz isparivača 311E-22 i 311E-19 provodi kroz izmjenjivače 311E-15 i 311E-13 u kojima se predgrijava sirovina.

Proizvod dna kolone 311D-7, teška frakcija FCC benzina, provodi se kroz vodeni hladnjak 311E-23, te pomoću crpke 311P-15 odvodi u spremište ili u daljnju obradu.

Tlak u koloni 311 D-7 regulira se pomoću PC-2A, koji djeluje na protok vršnih para iz kolone u kondenzator, dok se razina u koloni regulira pomoću regulatora razine LC-7, koji djeluje na protok proizvoda teške frakcije FCC benzina iz kolone.

3.5. Svojstva i odsumporavanje frakcija FCC benzina

Lagana frakcija FCC benzina, količine i sastava prikazanog tablicama 3 i 4 može se provoditi na daljnju obradu Merox procesom u kojem se iz lakog benzina ekstrahira merkaptanski sumpor.

Kako je prikazano tablicama 3 i 4, lagana frakcija FCC benzina dobivena preradom nafte tipa REB sadrži oko 300 ppm sumpora. To je većinom sumpor u merkaptanskim spojevima, te se iz benzina pomoću lužine može ekstrahirati i do 90 %. Dobrim vođenjem Merox postrojenja ukupan sumpor u lakoj frakciji može se smanjiti i ispod 50 ppm. U benzinu će, uz nešto merkaptanskog sumpora, zaostati tiofenski sumpor koji nije moguće ukloniti Merox procesom.

Lagana frakcija FCC benzina dobivena preradom nafte tipa Sirian light sadrži manji udio sumpora, pa je u nekim slučajevima moguće i direktno provođenje lagane frakcije u mješalište (blending) motornih benzina bez dodatne obrade.

Prilikom provođenja lagane frakcije FCC benzina s procesa Topping II na Merox postrojenje važno je voditi brigu o međuutjecajima postrojenja kako bi se izbjegle mogućnosti poremećaja i osigurao siguran rad.

Srednja frakcija FCC benzina, po svojim je svojstvima zahtjevna za daljnju obradu. Kako je vidljivo tablicama 3 i 4, frakcija ima nisku vrijednost oktanskog broja, a značajne udjele olefina, sumpora i dušika. Zbog velikog udjela olefina, frakcija je nezahvalna za hidroobradu na postojećim postrojenjima za desulfurizaciju s postojećim neselektivnim katalizatorima koji bi djelovali na daljnje smanjenje oktanskog broja. Srednja frakcija će se stoga provoditi na postrojenja Unifining II i Katalitički reforming u maksimalnoj mogućoj količini.

Teška frakcija FCC benzina, kako je vidljivo tablicama 3 i 4 ima značajan sadržaj sumpora. Oko 20 m^3/h teške frakcije obrađivat će se procesom hidrodesulfurizacije teške frakcije na revitaliziranom postrojenju 309HDS čija izvedba reaktora omogućava hlađenje reaktora plinom (quench plin), te se očekuje, ovisno o kriterijima vođenja procesa, smanjenje udjela sumpora na 50-100 ppm. Tešku frakciju FCC benzina, vrelište >165 °C, moguće je desulfurizirati i pomoću procesa Unifining I. Količina frakcije, vrelište >165 °C, je manja količina, a u težem rezu su u manjem udjelu zastupljeni olefini, pa izvedba reaktora bez dodavanja plina za hlađenje (quench) nije potrebna. Očekivani pad oktanskog broja teške frakcije FCC benzina (MOB+IOB)/2 je do 0.8.

4.0. Zaključci

Na osnovi eksperimentalnih podataka s industrijskih procesa pomoću programskog sustava za simuliranje procesa ChemCad 5.4. postavljeni su simulacijski modeli sljedećih procesa:

- sekcije za splitiranje i stabilizaciju postrojenja Topping II,
- sekcije atmosferske kolone BHK postrojenja,
- postrojenja 309HDS,

- postrojenja Unifining I.

Provedene su analize navedenih procesa s ciljem pronalaska optimalnog rješenja frakcionacije i hidroobrade FCC benzina. Kao kriteriji odabira optimalnog rješenja primijenjeni su: maksimalno smanjenje udjela sumpora, minimalni gubitak oktanskog broja i maksimalno iskorištenje postojeće opreme.

Na osnovi dobivenih podataka i provedene rasprave mogu se izvesti sljedeći zaključci:

– Sekcija za splitiranje i stabilizaciju postrojenja Topping II primjenjiva je u svrhu frakcionacije FCC benzina za kapacitet do 65 m^3/h na frakcije oba zahtijevana slučaja: laganu, <84 °C; srednju 84-132 °C; i tešku frakciju >132 °C, te laganu, <84 °C; srednju 84-165 °C; i tešku frakciju >165 °C. Frakcionacija je moguća uz preraspodjelu postojećih izmjenjivača topline kako je prikazano na slici 2 i korištenje lakog plinskog ulja s postrojenja Topping 3 kao ogrjevnog medija.

– Sekcija atmosferske kolone BHK postrojenja nije primjenjiva u svrhu frakcionacije FCC benzina bez zamjene postojećih kolona s većima.

– Postrojenje 309HDS s pripadajućim katalizatorom primjenjivo je za desulfurizaciju teške frakcije FCC benzina. Primjenom hidrodesulfurizacije smanjuje se udio sumpora s preko 2000 ppm, na 50-100 ppm.

– Postrojenje Unifining I nije preporučljivo primjenjivati u svrhu odsumporavanja teške frakcije FCC benzina, vrelišta >132°C, zbog izvedbe reaktora koji nema mogućnost hlađenja reaktora plinom koje je nužno zbog očekivanog velikog gradijenta temperature. Postrojenje Unifining I može odsumporavati količinski manje tešku frakciju, vrelišta >165, zbog manjeg gradijenta temperature kroz reaktor.

– Provedena istraživanja potvrđuju učinkovitost primjene matematičkog modeliranja i simuliranja u svrhe poboljšanja kvalitete proizvoda i optimizacije proizvodnje.

– Ostvarenje projekta očekuje se idućih mjeseci i primjer je unapređenja kvalitete proizvoda bez velikih ulaganja, a Rafineriji nafte Rijeka će doprinijeti većom količinom motornog benzina po europskim standardima.

IMPROVING GASOLINE QUALITY BY REDUCING THE FCC GASOLINE SULPHUR CONTENT

Abstract

Gasoline obtained through the process of fluid catalytic cracking is one among the largest sources of sulphur in gasoline production of the Rijeka OIl Refinery. Currently applicable standards allow for maximum sulphur content of 150 ppm, whereas the standard applicable as of 2005 will allow for the maximum of 50 ppm of gasoline sulphur content. Since the construction of units resolving the problem of sulphur is at the refinery not expected before 2006, a group of the refinery's experts has suggested a transitory solution through the use of the existing units for fractionation and desulphurization of FCC gasoline.

To this end, mathematical simulation models of the atmospheric distillation, unifining and HDS units have been set up. Researched and studied through simulation were the optimal operating conditions of the process, after which an optimal solution was suggested given the available process equipment, required capacities and required sulphur content reduction, as well as given the criteron of minimal loss of the gasoline octane number and the available volume of energents.

1.0. Introduction

Increasingly stringent environmental protection requirements have caused motor fuel manufacturers to improve their products' properties, among other things, also by reducing the gasoline sulphur content. The highest sulphur contribution to gasoline originates from the FCC gasoline, coking gasoline and heavy gasoline from the atmospheric distillation process, the highest source of sulphur being the FCC gasoline contributing as much as 40-90 % of sulphur to gasoline[5].

Reduction of the FCC gasoline sulphur content is obtained by:

(1) Hydrotreating FCC crude,
(2) Hydrotreating FCC gasoline.

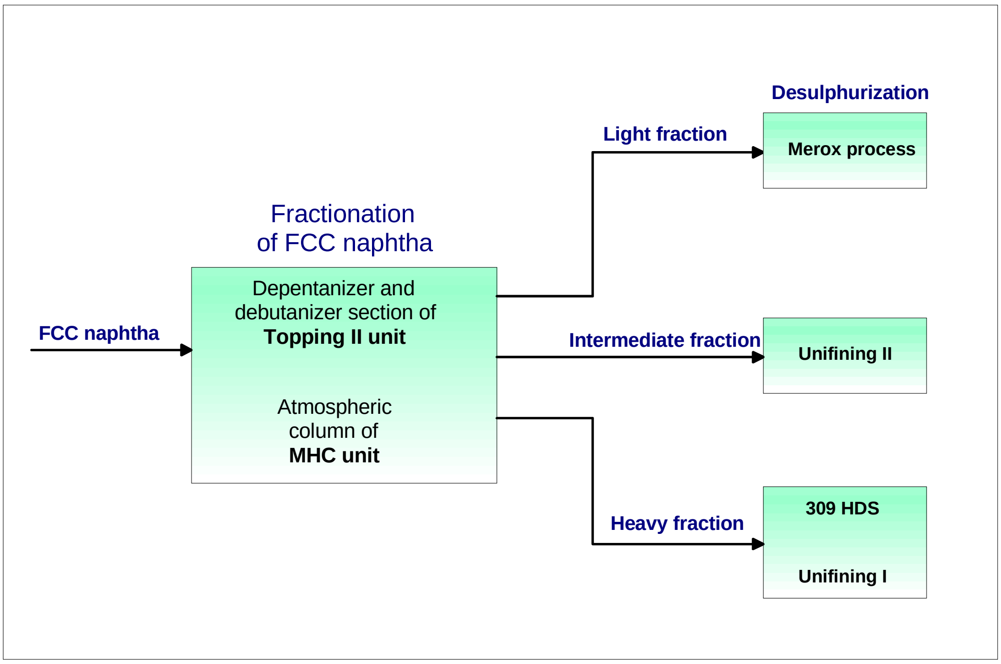
Hydrotreatment of the entire FCC gasoline fraction results in a considerable sulphur content reduction, but also in a considerable reduction of the octane number due to the saturation of olefins. It is a well-known fact that the share of olefins is higher in lighter fractions, while that of sulphur increases in heavier fractions, which is why FCC gasoline fractionation, followed by hydrotreatment of the heavy fraction, seems like a logical solution, resulting in only minimal octane number loss.[1]

Table 1: Gasoline properties according to European standards

	Maximum permissible sulphur concentration, ppm	
	Gasoline	Diesel fuel
European standard	EN-228	EN-590
1.1.2000.	150	350
1.1.2005.	50	50
1.1.2009.	10	10

Rijeka OIl Refinery has only limited possibilites of hydrotreating FCC feed on the HDS/MHC unit due to the need for a high volume of low sulphur diesel fuel, which is why the plant mostly operates as HDS. In addition, the construction of new units enabling a long-term solution for the quality of fuel with ultra low sulphur content is yet to be expected. It is necessary to achieve an adjustment to the European fuel quality standards as soon as possible, because, as of 1 January 2005, starts the application of the European standard EN-228 with a maximum permissible gasoline sulphur share of 50 ppm, Table 1. A group of the refinery's experts has suggested the idea of FCC gasoline fractionation on the mostly available units, followed by hydrotreatment of the obtained fractions, as shown in Figure 1.

Figure 1: Schematic presentation of possible solutions for FCC gasoline fractionation and desulphurization



2.0. The Experimental Part

Crude: FCC gasoline obtained through the processing of REB type crude, of composition as shown in Table 2.

FCC gasoline		REB
Density, g/cm³		0.735
Distillation		
	Beginning, °C	26.7
	5 % v/v, °C	33.9
	10 % v/v, °C	37.2
	20 % v/v, °C	44.0
	30 % v/v, °C	51.7
	40 % v/v, °C	62.6
	50 % v/v, °C	98.3
	60 % v/v, °C	103.7
	70 % v/v, °C	146.3
	80 % v/v, °C	158.1
	90 % v/v, °C	172.0
	95 % v/v, °C	182.7
	End °C, %v/v	209.4-98
Structural composition (FIA)		
Aromatics, %v/v		20.96
Olefins, %v/v		39.56
Paraffins + naphthenes, %v/v		38.88
Nitrogen content, mg/kg		39.21
Bromine no, mg/kg		60.41
Total sulphur content, %m/m		0.11
Octane no, RON		90.6
Octane no, MON		78.5

With the purpose of exploring the possibility of fractionating FCC gasoline, desulphurizing and processing the fractionation product by hydrogen on the existing units of the Rijeka Oil Refinery, the analysis of the following processes was performed[2]:

(1) Processes analyzed for the purpose of FCC gasoline fractionation:

- dependentanizer and debutanizer section of Topping II unit,
- atmospheric column of MHC unit.

(2) Processes analyzed for the purpose of hydrotreating the FCC gasoline heavy fraction:

- 309HDS,
- Unifining I.

Analysis of the processes was performed by creating simulation models based on experimental data from the industrial units. The mathematical simulation models have encompassed reactors, distillation columns, separators, heat exchangers, pumps and compressors. The software used while making the simulation models was ChemCad 5.4[3], with the simulation models of the Topping II and MHC units shown in Figures 2 and 3.

Figure 2. Simulation model of the depentanizer and debutanizer section of Topping II unit

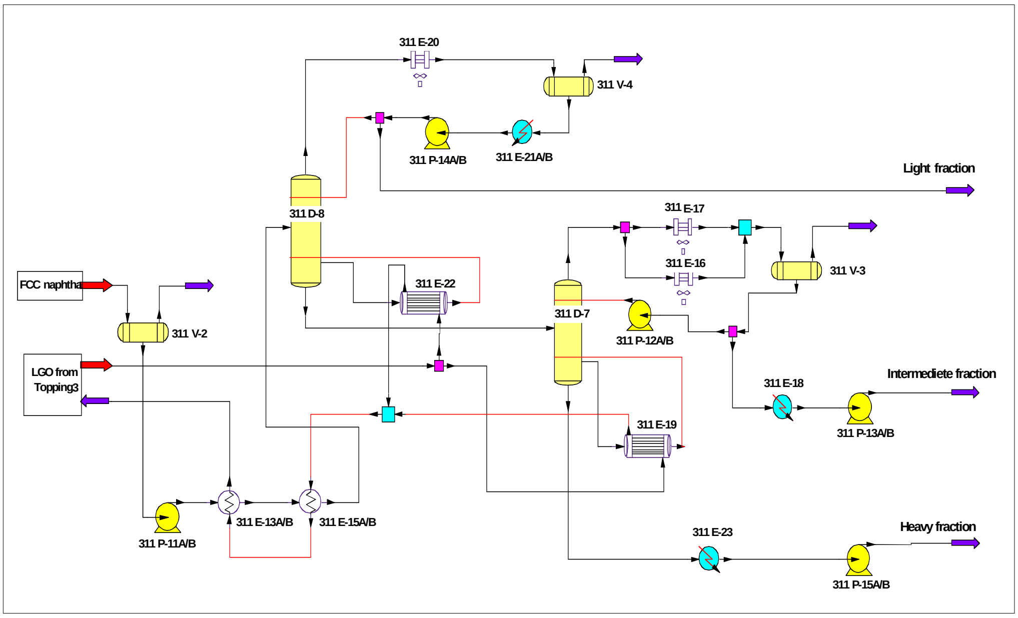
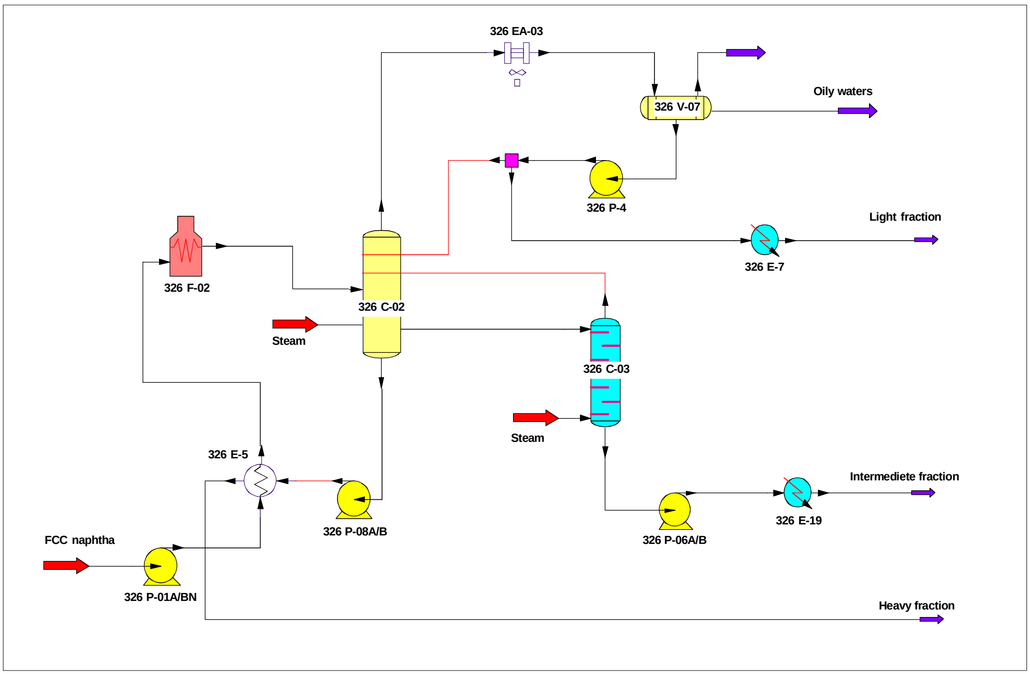


Figure 3. Simulation model of the atmospheric column of MHC unit



The analysis was performed for two crude types: REB and Sirian Light, for different crude flows (of 50 and 80 m^3/h) and for two fractionation cases:

Case 1.

- light fraction, flash point <84 °C,
- intermediate fraction, flash point 84-132 °C,
- heavy fraction, flash point >132 °C.

Case 2.

- light fraction, flash point <84 °C,
- intermediate fraction, flash point 84-165 °C,
- heavy fraction, flash point >165 °C,

As criteria for selecting the optimal solution applied were the following:

- maximum sulphur content reduction,
- minimal octane number lowering,
- maximal application of the available process equipement.

3.0. Results and Discussion

3.1. Possibilities of Applying the Existing Units for FCC Gasoline Fractionation

Fractionation possibilities were analyzed on MHC and Topping II units. The conducted analysis has shown that the existing MHC unit cannot be used for FCC gasoline fractionation without replacing columns 326C-02 and 326C-03 by those with larger diameter and higher number of trays.

Depentanizer and debutanizer section of Topping II unit can be used for FCC gasoline fractionation into products for both splitting cases[2]; case 1: light fraction, flash point <84 °C, intermediate fraction, flash point 84-132 °C, and heavy fraction, flash point >132 °C, and case 2: light fraction, flash point <84 °C, intermediate fraction, flash point 84-165 °C, and heavy fraction, flash point >165 °C. Depentanizer and debutanizer section of Topping II unit also enables fractionation between the said distillation cuts. Efficient fractionation requires unit adjustments by applying a more efficient preheating of the column 311D-8 feed.

3.2. Possibilities of Applying the Existing Units for FCC Gasoline Desulphurization

For the purpose of hydrotreatment and desulphurization of the FCC gasoline heavy fraction, flash point >132 °C, explored were the possibilities of applying the HDS and Unifining I units. FCC gasoline heavy fraction, flash point >132 °C, contains ca. 13 %v/v of olefins, which is why the application of 309HDS unit constitutes the only possible solution because of the reactor into which quench gas is introduced. The Unifining I unit does not have such a reactor, which is why olefin saturation generates a too high temperature gradient in it. That is why the hydrotreatment of the heavy fraction, flash point >132 °C, containing ca. 13 %v/v of olefins is not recommended on the existing Unifining I unit.

Intermediate fraction, flash point 84-132 °C, in the volume of 13 m^3/h, can be mixed with gasoline obtained through atmospheric distillation process and desulphurized on the Unifining II unit. Additional volume of 13 m^3/h does not exceed the permissible bromine number. Further processing on the catalytic reforming unit increases the gasoline octane number, with the production of highly necessary hydrogen.

Light fraction is taken to the Merox process for mercaptan removal, or, without additional processing, to the gasoline blending unit.

The possibility of applying the existing Unifining I plant for heavy fraction treatment has been analyzed assuming the treatment of the heavy fraction, flash point >155 °C. The heavy fraction, flash point >155 °C, contains ca. 10 %v/v of olefins. Reduced olefin content reduces also the temperature gradient within the reactor, thus enabling the treatment of thus produced fraction on the existing Unifining I unit.

Table 3: Chemical composition and properties of FCC gasoline fractions, for Case 1 fractionation

Process flow	FCC gasoline	Light fraction, <84 °C	Intermediate fraction, 84-132 °C	Heavy fraction, >132 °C
Flow, kg/h	47747.4	21020.3	9579.1	17148.0
Flow, m^3/h	65.8	32.6	13.3	20.6
Density, g/cm^3	0.735	0.662	0.750	0.837
Distillation				
Beginning, °C	26.7	25.6	95.3	145.8
5 % v/v, °C	33.9	32.0	98.2	151.5
10 % v/v, °C	37.2	33.8	98.6	151.9
20 % v/v, °C	44.0	36.9	99.6	154.0
30 % v/v, °C	51.7	39.9	100.7	157.1
40 % v/v, °C	62.6	43.2	101.4	159.8
50 % v/v, °C	98.3	46.7	102.2	163.0
60 % v/v, °C	103.7	50.4	104.2	168.5
70 % v/v, °C	146.3	54.6	106.3	173.6
80 % v/v, °C	158.1	59.9	108.7	180.0
90 % v/v, °C	172.0	66.6	113.4	188.9
95 % v/v, °C	182.7	71.4	117.9	196.5
End °C, %v/v	209.4-98	75.8-98	125.1-98	209.4-98
Structural composition (FIA)				
Aromatics, %v/v	20.96	0.00	12.72	59.92
Olefins, %v/v	39.56	57.89	36.46	13.12
Paraffins+naphthenes, %v/v	38.88	42.11	50.82	26.96
Nitrogen content, mg/kg	39.21	8.76	4.93	112.30
Bromine no, mg/kg	60.41	85.80	62.68	18.92
Total sulphur content, %m/m	0.11	0.03	0.12	0.23
Octane number, RON	90.6	-	87.5	92.8
Octane number, MON	78.5	-	75.0	81.0

Table 4: Chemical composition and properties of FCC gasoline fractions, for Case 2 fractionation

Process flow	FCC gasoline	Light fraction <84°C	Intermediate fraction 84-165°C	Heavy fraction >165°C
Flow, kg/h	47747.4	20708.0	18588.1	8451.3
Flow, m^3/h	65.8	31.7	24.2	9.9
Density, g/cm^3	0.735	0.662	0.777	0.861
Distillation				
Beginning, °C	26.7	25.9	101.8	174.9
5 % v/v, °C	33.9	31.2	107.9	177.5
10 % v/v, °C	37.2	33.1	110.2	178.1
20 % v/v, °C	44.0	36.3	113.1	179.0
30 % v/v, °C	51.7	39.7	115.1	180.2
40 % v/v, °C	62.6	43.2	117.5	181.2
50 % v/v, °C	98.3	46.9	121.1	182.5
60 % v/v, °C	103.7	51.0	125.9	184.1
70 % v/v, °C	146.3	55.6	131.5	186.6
80 % v/v, °C	158.1	61.2	137.8	190.5
90 % v/v, °C	172.0	68.2	145.0	196.8
95 % v/v, °C	182.7	73.7	150.2	202.5
End °C, %v/v	209.4-98	78.7-97	156.1-98	217.4-98.5
Structural composition (FIA)				
Aromatics, %v/v	20.96	0.00	29.00	71.84
Olefins, %v/v	39.56	60.20	27.48	7.89
Paraffins + naphthenes, %v/v	38.88	39.80	43.52	20.27
Nitrogen content, mg/kg	39.21	7.80	17.93	186.00
Bromine number, mg/kg	60.41	85.33	43.98	13.80
Total sulphur content, %m/m	0.11	0.04	0.16	0.26
Octane number, RON	90.6	-	88.0	93.7
Octane number, MON	78.5	-	75.6	82.3

3.3. Optimal Solution for FCC Gasoline Fractionation

Optimal solution for FCC gasoline fractionation is based on the following:

- utilization of the existing equipment,
- adjustment of fractionation and synthesis of the unit's layout with the purpose of maximizing the utilization level of the existing process equipment capacities,
- maximizing the utilization level of the available thermal energy.

The greatest drawback of applying the depentanizer and debutanizer section of Topping II unit for the purpose of fractionation is the impossibility of medium heating using the furnace. Process analysis using simulation model has suggested an optimal distribution of heat exchangers for the purpose of maximum heat use. Used as the heating medium is light gas oil conducted from the Topping III unit. Limited volume of LGO conditions maximum fractionation capacity of 65 m^3/h, as shown in Table 3. Tables 3 and 4 show the volumes and properties of products obtained through fractionation using the Topping II unit.

3.4. Description of the Optimal Fractionation Solution Process

The crude, FCC gasoline, is introduced from the reservoir into the crude feed vessel 311 V-2. Fluid level in the vessel is regulated using a LC-3 level regulator cascadely connected to the flow regulator FC-3, regulating the flow of FCC gasoline into the fractionation process. Left over process water is separated in water separator, vessel 311V-2. Water level is regulated using LDC-2 level regulation.

Through the pump 311 P-11A/B, FCC gasoline is conducted, through heat exchangers 311E-13 and 311E-15, in which the crude is preheated using light gas oil. Heated up to 138 °C, it is introduced into the 21st and 23rd plate of column 311D-8. In column 311D-8, light FCC gasoline is separated from heavier fractions. At the top of column 311D-8 top vapour is separated, condensed in air condenser 311E-20, and in liquid form conducted into reflux input vessel 311V-4. Liquid hydrocarbons from the vessel are additionally cooled through the air cooler 311E-21, and then, using pump 311P-14A/B, partially return into the column as reflux, while the remaining volume of liquid hydrocarbons is as light fraction of FCC gasoline conducted into the reservoir or for further processing.

Pressure in vessel 311 V-4 is regulated using pressure regulator PC-3B, and the level using level regulator LC-6, impacting the flow of the FCC gasoline light fraction products. The flow of the reflux into the stripper is regulated using flow regulator FC-10.

Liquid hydrocarbons from the bottom of column 311 D-8 partially evaporate in the evaporizer 311E-22 using light gas oil, whose flow is regulated using FC-13. Evaporated hydrocarbons are introduced into the bottom of the column, while the product from the bottom of the stripper is conducted into column 311 D-7.

The level in column 311 D-8 is regulated using level regulator LC-4, impacting the flow of the column bottom products, while the pressure is regulated using pressure regulator PC-3A, causing the top vapour to flow into the reflux collecting vessel.

From the top of column 311D-7 vapours are conducted through paralelly connected air condensers 311E-16 and 311E-17, and collected in liquid form in the reflux collecting vessel 311V-3.

The pressure in vessel 311V-3 is regulated using pressure regulator PC-2B.

Liquid hydrocarbons from the vessel 311V-3 are partially returned into the column as reflux using pump 311 P-12, while the remaining part, intermediate fraction of FCC gasoline is, using the pump 311P-13, through the refrigerator 311E-18, conducted into the reservoir. The level in the reflux collecting vessel is regulated using level regulator LC-5, impacting the flow of the FCC gasoline intermediate fraction products.

At the bottom of column 311D-7, liquid hydrocarbons are separated and then partially evaporated in the evaporizer 311E-19, through heating using light gas oil. LGO flow is regulated using flow regulator FC-12. Evaporated hydrocarbons return to the bottom of column 311 D-7.

LGO from the evaporizers 311E-22 and 311E-19 is conducted through exchangers 311E-15 and 311E-13 in which the crude is preheated.

Product from the bottom of column 311D-7, heavy fraction of FCC gasoline, is conducted through water cooler 311E-23, and, using pump 311P-15, taken to the reservoir or for further processing.

The pressure in column 311 D-7 is regulated using PC-2A, causing the top vapour from the column to flow into the condenser, while the level in the column is regulated using the level regulator LC-7, impacting the flow of the FCC gasoline heavy fraction products from the column.

3.5. Properties and Desulphurization of FCC Gasoline Fractions

Light fraction of FCC gasoline, in the volume and of the composition as shown in Tables 3 and 4, may furtherly undergo Merox process in which mercaptan sulphur is extracted from light naphtha.

As shown in Tables 3 and 4, light fraction of FCC gasoline, obtained by processing crude of type REB, contains around 300 ppm of sulphur. It is mostly sulphur in mercaptan compounds, which is why, using alkali, up to 90 % of it may be extracted. Proper operation of the Merox unit may reduce total sulphur content in the light fraction down to below 50 ppm. Along with some mercaptan sulphur, there shall remain also some tiophene sulphur which cannot be removed by the Merox process.

Light fraction of FCC gasoline, obtained by processing crude of the type Sirian light, contains a lower share of sulphur, so that in some cases the light fraction may proceed directly to blending, without any additional processing.

While conducting the light fraction of FCC gasoline from the Topping II unit to the Merox process, it is important to take care of the mutual influence of the two units in order to avoid any possibility of failure and ensure safe operation.

Intermediate fraction of FCC gasoline is, due to its properties, rather demanding for further processing. As shown in Tables 3 and 4, the fraction has a low octane number value, and considerable shares of olefins, sulphur and nitrogen. Due to a high olefin share, the fraction is not suitable for hydrotreatment on the existing desulphurization plants with the existing unselective catalysts which would cause a further octane number lowering. Intermediate fraction shall therefore be conducted to the Unifining II and catalytic reforming units in the maximum available quantity.

Heavy fraction of FCC gasoline, as shown in Tables 3 and 4, has a considerable sulphur content. Some 20 m^3/h of the heavy fraction shall be processed by hydrodesulphurization on the revitalized unit 309HDS whose reactor enables gas quenching. It is expected – depending on the process conductance criteria - that the sulphur share shall be reduced down to 50-100ppm. Heavy fraction of FCC gasoline, its flash point being >165 °C, may also be desulphurized using the Unifining I unit. The volume of the fraction with the flash point >165 °C is lower, while, in the heavier cut, there is a lower share of olefins, which is why the reactor design with quench gas addition is not necessary. The expected octane number reduction of the heavy fraction of FCC gasoline (RON+MON)/2 is up to 0.8.

4.0. Conclusion

Based on experimental data from the industrial units, using the ChemCad 5.4 process simulation software, simulation models have been set up for the following:

- dependanizer and debutanizer section of Topping II unit,
- atmospheric column of MHC unit,
- 309HDS unit,
- Unifining I unit.

Analyses were performed of the said processes with the purpose of finding an optimal solution for the fractionation and hydrotreatment of FCC gasoline. Applied were the following criteria of selecting an optimal solution: maximum reduction of the sulphur content, minimal loss of the octane number and maximum utilization level of the existing equipment.

Based on the data obtained and the discussion conducted, the following conclusions may be drawn:

- Depentanizer and debutanizer section of Topping II unit may be applied for the fractionation of FCC gasoline, for the capacity of up to 65 m^3/h, into fractions of both required cases: light, <84 °C; intermediate 84-132 °C; and heavy fraction >132 °C, and light, <84 °C; intermediate 84-165 °C; and heavy fraction >165 °C. Fractionation is possible assuming a redistribution of the existing heat exchangers, as shown in Figure 2, and using light gas oil from the Topping 3 unit as a heating medium.
- Atmospheric column of MHC unit cannot be applied for the fractionation of FCC gasoline without a previous replacement of the existing columns by bigger ones.

- The 309HDS unit with its catalyst may be applied for the desulphurization of heavy fraction of FCC gasoline. By applying hydrodesulphurization, the sulphur content is reduced from over 2000 ppm down to 50-100 ppm.
- It would not be advisable to use the Unifining I unit for the purpose of desulphurization of heavy fraction of FCC gasoline with flash point >132 °C, because of the reactor that cannot be quenched by gas, which would be necessary due to the expected high temperature gradient. The Unifining I unit may be used for the desulphurization of the heavy fraction with flash point >165, lower in volume, owing to the lower temperature gradient through the reactor.
- Conducted research has confirmed the efficiency of applying mathematical modelling and simulation for the purpose of advancing product quality and optimizing production.
- The project's implementation is expected over the next several months, as an example of advancing product quality without any major investments, while at the same time enabling the Rijeka Oil Refinery to produce higher volumes of gasoline matching European standards.

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UDK/UDC	Ključne riječi	Key words
665.733.5.033.52	sadržaj sumpora u motornom benzinu	sulfur content of motor gasoline
665.733.5.035.3	anti-knock indeks benzina (IOB+MOB)/2	gasoline anti-knock index (RON+MON)/2
519.2.001.57	matematički simulacijski model	mathematical simulation model
665.658.26	hidrodesulfurizacija teškog FCC benzina	heavy FCC gasoline hydrodesulfurization postreatment
665.658.26	Unifining teških i srednjih FCC benzina	heavy and middle FCC gasoline Unifining postreatment
665.666.4	Merox lakog FCC benzina	light FCC naphta Merox posttreatment

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