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REFORMULIRANJE MOTORNIH BENZINA SUKLADNO BUDUĆIM ZAHTJEVIMA KVALITETE

Sažetak

Zakonske regulative propisuju kvalitetu motornih goriva s ciljem smanjenja ukupne emisije koja nastaje njihovom uporabom. Dostizanje dogovorenih standarda emisije na području transporta moguće je postići sinergističkim djelovanjem na kvalitetu goriva i izvedbu vozila. Ukoliko se govori o motornim benzinima, ključni parametri kvalitete koji se moraju korigirati su sadržaj sumpora, benzena, aromata, olefina i tlak para.

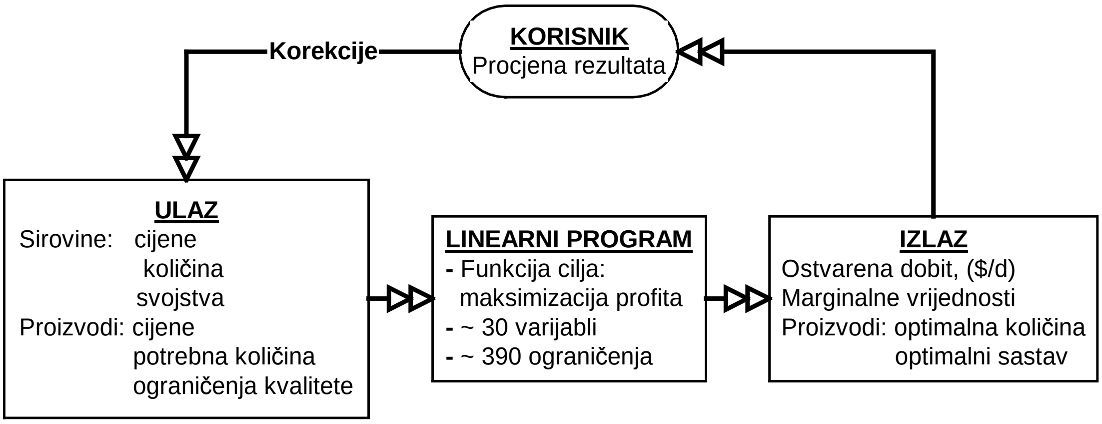
U ovom radu razmatran je utjecaj fizikalno kemijskih svojstava optimalno formuliranog motornog benzina BMB 95 na ukupnu emisiju prekursora troposferskog ozona. Postupna prilagodba formulacije motornog benzina postavljenim budućim zahtjevima kvalitete (trenutačne specifikacije u INI i prijedlog EU nakon 2005. godine) praćena je izračunom emisije organskih komponenti, dušikovih oksida i toksičnih tvari za svaki razmatrani slučaj. Za izračun emisija korišten je model postavljen od Energy Information Administration, U.S. Department of Energy. Matematički model namješavanja motornih benzina formiran je tehnikom linearnog programiranja uz definirana ograničenja koja su potrebna da bi se zadovoljila buduća kvaliteta.

Uvod

Auto Oil Program, koji je sredinom 1996. godine predstavila Komisija EU, određuje granice dopuštene emisije iz motornih vozila te uvjetuje kvalitetu motornih goriva (1,2). Na temelju ispitivanja provedenih programom, definirani su kritični parametri kvalitete goriva na osnovi kojih su utvrđene europske specifikacije goriva. Specifikacije kvalitativno i kvantitativno određuju strukturno-grupni sastav goriva uz vrlo stroge zahtjeve u vezi ograničenja sadržaja sumpora.

Zbog zadanih ograničenja postizanje glavnih primjenskih svojstava goriva (oktanski i cetanski broj) pred rafinerije postavlja zahtjeve formuliranja goriva koja svojim sastavom zadovoljavaju i specifikacije sastava i osnovne zahtjeve primjenskih svojstava. Ograničenje sadržaja sumpora u motornim gorivima je dodatni čimbenik koji bitno određuje kvalitetu goriva i usmjerava tehnološki razvoj rafinerija. Zbog toga optimiranje namješavanja motornih goriva, kojemu je cilj postizanje definiranih parametara kvalitete uz prihvatljivu ekonomičnost, predstavlja vrlo važan čimbenik u proizvodnji goriva, posebno u slučaju ograničenih resursa pojedinih komponenti za namješavanje (3,4,5).

Slika 1: Blok shema LP modela
Figure 1: LP model Block Diagram



Corrections

USER
Results estimation

INPUT
Feeds: prices
quantity
properties
Products: prices
necessary volumes
quality limitations

LINEAR PROGRAMME
- Goal function:
profit maximization
- ≈ 30 variables
- ≈ 390 limitations

OUTPUT
Profit raised ($/d)
Marginal values
Products: optimal volumes
optimal composition

LP-model

Namješavanje motornih benzina je klasični problem pronalaženja optimuma definirane funkcije cilja koji se može riješiti metodom linearnog programiranja. Ograničenja koja se definiraju pri rješavanju problema namješavanja odnose se na količine i specifična svojstva benzina, dok je funkcija cilja postavljena kao maksimizacija profita (6). LP-model koji je korišten u ovome radu sastoji se od tri međusobno povezana dijela kao što se može vidjeti na slici 1.

Na raspolaganju je 8 sirovina za koje je potrebno definirati: cijenu ($/bbl, $/t,), raspoloživu količinu (bbl,t) kao i svojstva: IOB, MOB, sumpor (mas.%), aromati (vol.%), olefini (vol.%), benzen (vol.%), kisik (mas.%), RVP (hPa), gustoća (g/cm^3), karakteristične točke destilacije (E70 ^{0}C, E100 ^{0}C, E180 ^{0}C, E215 ^{0}C)(7). Model omogućava namješavanje tri različita motorna benzina za koje je potrebno unijeti: cijenu ($/bbl, $/t,), granice unutar kojih se nalazi tražena količina (bbl,t) te specificirati minimalnu vrijednost istraživačkog i motornog oktanskog broja, maksimalnu količinu sumpora, aromata, olefina, benzena i kisika te specificirati granice unutar kojih će se nalaziti gustoća, RVP i karakteristične točke destilacije (E180 ^{0}C i E215 ^{0}C su ograničene samo minimalnim vrijednostima).

Unos podataka koji se odnose na sirovine i proizvode je ostvaren u tablicama pisanim u MS Excelu. Program je kreiran u programskom jeziku LINGO, LINDO Systems Inc i sastoji se od 27 varijabli i 390 ograničenja (8). Program je koncipiran tako da je moguće uz neznatne preinake povećati broj sirovina i proizvoda te uvesti nova ograničenja svojstava i količina. Rezultati riješenog problema se ispisuju u standardnom LINGO obliku (*Solution Report*), koji pored optimalne formulacije proizvoda daje i strukturu marginalnih vrijednosti (*DP-Dual Price*[*]). Osim toga, rješenja se ispisuju i u MS Excelovu tablicu iz koje se ti rezultati povlače i koriste za izračun karakterističnih svojstava proizvoda.

Računanje emisije

Početkom devedesetih godina *Environmental Protection Agency* (EPA) je propisala uredbu koja postavlja kriterije kvalitete goriva i strategiju njegovog

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[*] Dual Price je vrijednost koja se odnosi na svako ograničenje u modelu, a može se interpretirati kao vrijednost za koju će se povećati funkcija cilja (tj. smanjiti ako je negativna) povećanjem desne strane ograničenja za jediničnu vrijednost.

daljnjeg unapređenja koja bi jamčila postupno smanjenje emisije prekursora troposferskog ozona (smoga) u devet urbanih zona širom SAD (9,10).

Da bi se provela takva uredba, napravljen je model koji na osnovi karakterističnih svojstava benzina izračunava emisije hlapljivih komponenti i ispušnih plinova. Model se sastoji od 15 nelinearnih jednadžbi koje su dobivene obradbom rezultata istraživanja provedenih unutar američkog. Auto/Oil* programa. Kao referentno gorivo korišten je motorni benzin (*Baseline Fuel* koji predstavlja prosječnu kvalitetu goriva u SAD za ljeto 1990.) čije su karakteristike prikazane u tablici 1 (11).

Tablica 1: Karakteristike referentnog goriva
Table 1: Reference Fuel Characteristics

Gustoća/Density, kg/dm^3	0,749
(IOB+MON)/2 / (RON + MON)/2	87,3
Kisik/Oxygen, mas. %	0
RVP, hPa	600
Benzen, vol. %	1,53
Aromati, vol. %	32
Olefini, vol. %	9,2
Sumpor/Sulphur, ppm	340
T 50, ^{0}C (maks.)	103
T 90, ^{0}C (maks.)	165

Jednadžbe kojima su opisane ovisnosti između fizikalno-kemijskih svojstava i emisije mogu se svrstati u tri skupine i to:

- sedam jednadžbi koje služe za računanje emisije ispušnih plinova i to:
  - organskih komponenata (VOC – *Volatile Organic Compound*)
  - dušikovih oksida - NO_x
  - toksičnih tvari (benzena, 1,3-butadiena, formaldehida, acetaldehida i poliaromatskih ugljikovodika)
- Četiri jednadžbe pomoću kojih se računaju emisije hlapljivih organskih tvari:
  - emisije iz zaustavljenog vozila s hladnim motorom – *diurnal losses*
  - emisije iz zaustavljenog vozila sa zagrijanim motorom – *hot-soak losses*
  - emisije iz vozila u pokretu – *running losses*
  - emisije hlapljivih komponenata koje nastaju pri punjenju spremnika vozila

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* "Auto/Oil Air Quality Improvement Research Program"

- Četiri jednadžbe za računanje emisije benzena koja nastaje pri evaporaciji (emisija benzena pri isparavanju odnosi se na četiri gornja slučaja).

Tablica 2: Utjecaj fizikalno-kemijskih karakteristika benzina na emisiju
Table 2: Impact of Gasoline Physical and Chemical Properties on Emissions

	Ispušni plinovi/Exhaust gases			Evaporacija	
Parametri	VOC	NO_x	Toksične tvari/Toxic	VOC	Benzen
RVP	✓	✓	✓	✓	✓
$(RVP)^2$				✓	✓
$(RVP)^3$					✓
Kisik/Oxygen	✓	✓	✓		
Aromati	✓	✓	✓		
$(\text{Aromati})^2$		✓			
Benzen			✓		✓
Olefini	✓	✓	✓		
$(\text{Olefini})^2$		✓			
Sumpor/Sulphur	✓	✓	✓		
$(\text{Sumpor/Sulphur})^2$		✓			
E 200 ^{0}F *	✓	✓	✓		
$(E\ 200\ ^0F)^2$	✓				
E 300 ^{0}F *	✓		✓		
$(E\ 300\ ^0F)^2$	✓				
(Aromati) x (E 300 ^{0}F)	✓				
MTBE			✓		✓
ETBE			✓		
Etanol			✓		

*postotak predestiliranog na 200 ^{0}F (93 ^{0}C), odnosno na 300 ^{0}F(148 ^{0}C).
*percentage of the volume predistilled at 200 ^{0}F (93 ^{0}C), i.e. 300 ^{0}F (148 ^{0}C).

U tablici 3 prikazani su parametri ovih nelinearnih jednadžbi, tj. utjecaj svojstva benzina na pojedinu emisiju. Model koji je korišten u ovom radu temeljen je na ovisnostima koje su iznesene u tablici 2, a izradio ga je *Energy Information Administration, U.S. Department of Energy* (9,10). Ugradnja modela za izračun emisije u model za optimalno namješavanje motornih benzina je ostvarena unutar MS-Excela te nije moguće provesti optimiranje sastava benzina na osnovi ograničenja koja čine model za računanje emisije.

Postavljanje početnih uvjeta

Rad je zamišljen tako da se, počevši od važećih specifikacija kvalitete goriva[*], postupnom prilagodbom pojedinih svojstava (RVP, sumpor, benzen,

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[*] Kvaliteta propisana Ininom internom normom.

aromati i olefini) formulira motorni benzin koji bi zadovoljio europsku kvalitetu u 2005. godini. U tom smislu napravljeno je osam formulacija BMB95, koje unutar definiranih ograničenja predstavljaju optimalni sastav, te je uspoređena ukupna emisija organskih komponenata, emisija organskih tvari kroz ispušne plinove, emisija dušikovih oksida i emisija toksičnih tvari. Pored toga uspoređena je i ukupna zarada kao i ukupna količina namiješanog benzina za svaki pojedini slučaj.

Kao početni slučaj uzeta je kvaliteta sirovina za namješavanje te sastav benzina koji je dobiven kao optimalno rješenje rafinerijskog LP modela za RN Rijeka (12). Za promatrani slučaj uzete su dvije nafte *Iranian heavy*, 63,5% i *Brent*. Uzeta je cijena *Brenta* 26 $/bbl (197 $/t) iz koje su izvedene i cijene proizvoda. Količine sirovina za namješavanje motornih benzina uzete su uz pretpostavku iskorištenih 80-90% preradbenih kapaciteta postrojenja u RN Rijeka, dok su količine kao i svojstva sirovina koje se trenutačno ne proizvode određene na osnovi literaturnih podataka (7,9,13,14). Cijene, raspoložive količine i fizikalno kemijske karakteristike sirovina za namješavanje prikazane su u tablicama 3 i 4.

Tablica 3: Sirovine preuzete iz LP modela RN Rijeka
Table 3: Feeds taken over from Rijeka Oil Refinery LP Model

	C_4-frakcija	i-pentan	n-C_5^+	FCC benzin	REF-98	REF-100	HO-VBKben[1]	MTBE
Cijena/Price, $/t	268.52	180.13	157.54	281.25	327.09	332.75	337.50	400.00
Cijena/Price, $/bbl	26.05	18.19	16.25	32.87	40.94	42.03	37.56	47.43
Raspoloživost/Availability,t/d	165	300	300	1350	200	1300	60	50
Raspoloživost/Availab.,bbl/d	1700.508	2970.297	2907.989	11551.672	1597.891	10292.170	539.151	421.645
RON	99	78.5	75.9983	92.5	97.9	99.8	93.5	110
MON	84.7	76	73.4331	80.5	88.6	90.6	81.5	101
Sumpor/Sulphur, mas.%	0	0	0.0019	0.2504	0	000	0	0
Aromati, vol.%	0	0	0.3175	20	64.9	65.3	3	0
Olefini, vol. %	83.0303	0	0	35	0	0	0	0
Benzen,vol. %	0	0	0.3175	0.55	2.79	2.88	00	0
Kisik/Oxygen, mas. %	0	0	0	0	0	0	0	18.2
RVP, hPa	4099.6073	986.9	797.2952	445.1	460.3	541.7	445	560
RVP-indeks	32804.077	5531.481	9334.995	2044.429	2132.069	2613.356	2043.855	2724.175
Gustoća/Density, g/cm3	0.6103	0.6353	0.6489	0.7351	0.7873	0.7945	0.7	0.7459
E70 ^{0}C, vol. %	100	99.8	100	32.4	26.1	27.4	32	100
E100 ^{0}C, vol. %	100	100	100	52.2	40	41.2	52	100
E180 ^{0}C, vol. %	100	100	100	93.2	98.3	98.6	93	100
E215 ^{0}C, vol. %	100	100	100	100	100	100	100	100

[1] - Hidroobrađeni visbreaking benzin/[1]Hydrotreated visbreaking gasoline

Osnovna ograničenja koja onemogućuju namješavanje motornih benzina prema budućim zahtjevima kvalitete odnose se na sumpor i benzen. U tom smislu u ovom radu razmatrano je nekoliko tehnoloških opcija koje rješavaju te probleme.

Kako FCC benzin u najvećoj mjeri (čak i do 98%) doprinosi količini sumpora u ukupnom benzinskom poolu, to rješavanje problema sumpora u motornim benzinima znači uklanjanje sumpora iz FCC benzina (15, 16).

Tablica 4: Sirovine koje se trenutačno ne rabe u RN Rijeka
Table 4: Feeds currently not processed in Rijeka Oil Refinery

	FCC(1) benzin[1]	FCC(2) benzin[2]	i-$C_{5(\check{c}isti)}$	Izomerat	Ref.-spliter	Alkilat
Cijena/Price, $/t	290.85	311.90	237.50	250.00	346.25	362.50
Cijena/Price, $/bbl	34.2	36.5	23.03	25.56	44.59	40.46
Raspoloživost/Availability, t/d	1350	1400	300	800	970	500
Raspoloživos/Availability, bbl/d	11712.599	12146.399	3093.492	7825.940	7532.588	4480.128
RON	89.5	92.2	92	83	104	94
MON	78.5	80.2	89	82	94	92
Sumpor/Sulphur, mas.%	0.01	0.01	0	0	0	0
Aromati, vol.%	20	20	0	0	80	0
Olefini, vol. %	10	35.9	0	0	0	1.0
Benzen,vol. %	0.55	0.55	0	0	0	0
Kisik/Oxygene, mas. %	0	0.0	0	0	0	0
RVP, hPa	470	470	986.9	780	350	186
RVP-indeks	2188.378	2188.378	5531.481	9334.995	1513.858	686.896
Gustoća/Density, g/cm3	0.7250	0.7250	0.6100	0.6430	0.810	0.7020
E 70 ^{0}C, vol. %	32.4	32.4	99.8000	98	8	8.
E 100 ^{0}C, vol. %	52.2	52.2	100	100	25	28.
E 180 ^{0}C, vol. %	93.2	93.2	100	100	95	95.
E 215 ^{0}C, vol. %	100	100	100	100	100	100

[1] FCC benzin koji je naknadno podvrgnut hidroobradi/[1] FCC gasoline subsequently subjected to hydrotreatment

[2] FCC benzin dobiven katalitičkim krekiranjem hidrodesulfurizirane sirovine/[2] FCC gasoline obtained through the catalytic cracking of hydrodesulphurized feed

Ukloniti sumpor iz FCC benzina moguće je na jedan od sljedeća četiri načina:

- prerada niskosumporne nafte
- smanjenje završne točke destilacije FCC benzina
- naknadna hidroobrada FCC benzina
- hidrodesulfurizacija FCC sirovine

Prva dva rješenja su kratkoročna i ekonomski neisplativa zbog više cijene niskosuporne nafte u prvom slučaju, te gubitka oktana i količine sirovine za namješavanje u drugom slučaju. U ovom radu razmatrana su samo dva posljednja slučaja. Prema podacima preuzetim iz rafinerijskog LP modela za već spomenute nafte FCC sirovina sadrži 1,255% sumpora što rezultira količinom sumpora u FCC benzinu od 0,2504 mas.%. Za slučaj naknadne hidroobrade FCC benzina karakteristično je smanjenje oktanske vrijednosti kao i promjena drugih svojstava što se može vidjeti iz tablice 4. Cijena kao i svojstva FCC benzina koji je podvrgnut 95%-tnoj hidrodesulfurizaciji uzeti su iz literature (13,14,15,16,17). Predobrada FCC sirovine, iako skuplji proces, u odnosu na prethodni slučaj ima nekoliko bitnih prednosti:

- neznatno smanjenje oktanskog broja
- povećana konverzija FCC procesa
- na ovaj način uklanja se sumpor iz svih proizvoda FCC-a.

U tablici 4 dana je cijena i svojstva FCC benzina dobivenog krekiranjem hidrodesulfurizirane sirovine. Prekursori benzena u benzinskom *poolu* su reformat benzin (oko 81%) i FCC benzin (oko 17%). Primjenjujući sličnu strategiju kao i kod uklanjanja sumpora, potrebno je smanjiti sadržaj benzena u reformat benzinu, a to je moguće na jedan od sljedećih načina (18):

- frakcioniranjem sirovine za reforming (teški primarni benzin) tako da se isključi temperaturno područje vrenja benzena.
- smanjenjem tlaka u reformeru
- splitiranjem reformata te hidrogenacija benzena, tj. vršnog produkta splitiranja.

Prvi slučaj traži najmanje troškove, međutim, tim postupkom snižava se vrijednost oktanskog broja reforming benzina. Pored toga prefrakcioniranjem sirovine za reforming nemoguće je zadovoljiti buduće ograničenje benzena u motornim benzinima od maks. 1 vol.%. Druga opcija također nije zadovoljavajuće rješenje, jer se na taj način smanjuje proizvodnja vodika, smanjuje konverzija kao i oktanski broj reformata te se povećava količina istaloženog koksa na katalizatoru. U ovom radu razmatrana je opcija uklanjanja benzena hidrogeniranjem uz prethodno splitiranje reformata, nakon čega bi zasićeni produkti poslužili kao sirovina za izomerizaciju (UOP *Penex/DIH* proces).

Prilikom optimiranja namješavanja benzina koji zadovoljava specifikacije za 2005. godinu kao visoko vrijedna sirovina upotrijebljen je alkilat (slučaj 7). U završnom slučaju prikazana je optimalna formulacija reformuliranog benzina prema specifikacijama propisanim unutar Phase II*.

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* Kvaliteta reformuliranog motornog benzina definirana Uredbom EPA Clean Air Act (CAA), koja je na snazi u SAD od 1. siječnja 2000.

Rasprava

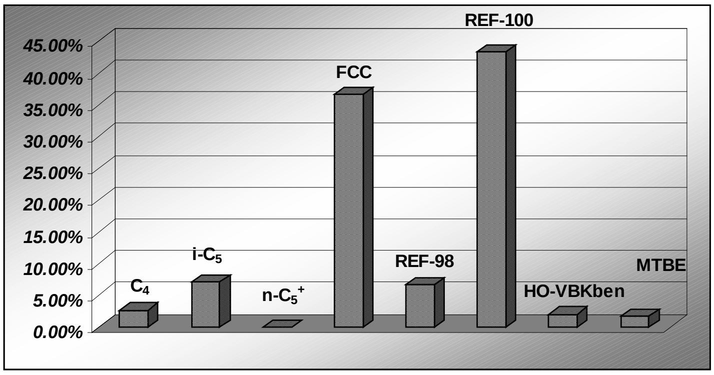
Početni slučaj je optimalna formulacija bezolovnog motornog benzina koji zadovoljava trenutačne specifikacije koje su propisane Ininom internom normom. Struktura sastava benzina te nastale emisije prikazane su na slici 2, odnosno slici 10, dok su fizikalno-kemijske značajke prikazane u tablici 5.

Tablica 5: Specifikacije namiješanih benzina za svaki pojedini slučaj
Table 5: Specifications of gasoline for each particular case

	Slučaj/Case							
	Počet/Initial	2	3	4	5	6	7	8
RON, min	95.2	95.2	95.2	95.2	95.2	96.9	95.2	96.5
MON, min	85.3	85.7	85.7	85.2	85.4	87.6	86.3	85.2
Sumpor/Sulphur(maks.),ppm	990.0	30.1	30.1	40.8	50.0	36.0	41.0	33.2
Aromati (maks.), vol. %	38.36	43.66	43.66	39.83	33.74	35.00	34.72	25.00
Olefini (maks.), vol. %	15.82	4.14	4.14	16.20	18.74	13.19	15.00	12.00
Benzen (maks.), vol. %	1.56	1.81	1.81	1.61	0.56	0.44	0.47	0.65
Kisik/Oxygen(maks.),mas.%	0.30	0.36	0.36	0.31	0.00	1.78	0.27	2.00
RVP, hPa	700.0	600.0	600.0	600.0	600.0	600.0	600.0	546.1
RVP-indeks	3600.58	2969.54	2969.54	2969.54	2969.54	2969.54	2969.54	2639.95
Gustoća/Density, g/cm3	0.750	0.757	0.757	0.751	0.731	0.741	0.737	0.725
E 70 ^{0}C, vol. %	38.89	35.65	35.65	36.41	37.90	42.27	36.14	45.00
E 100 ^{0}C, vol. %	53.26	50.22	50.22	51.44	53.28	55.95	51.39	58.40
E 180 ^{0}C, vol. %	96.63	96.89	96.89	96.43	95.25	95.88	95.45	96.17
E 215 ^{0}C, vol. %	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

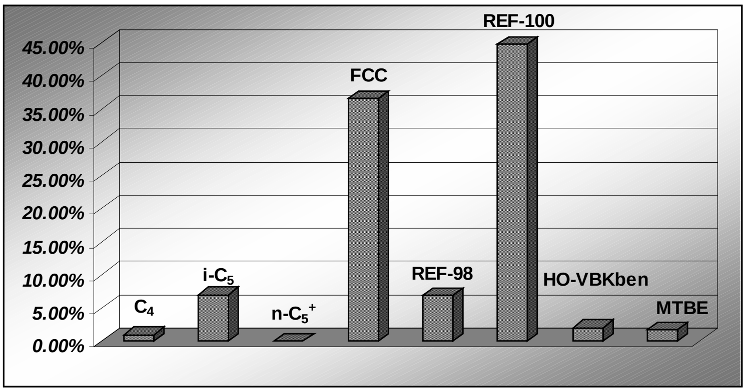
Ograničenje minimalne vrijednosti oktanskog broja je temeljno ograničenje u modelu što potvrđuju i visoke marginalne vrijednosti (*Dual Price*) visoko oktanskih komponenata (DP_{MTBE}=110,6 $/t, $DP_{REF\text{-}100}$=48,6 $/t). Ograničenje sumpora na 990 ppm limitira količinu FCC benzina tako da je 18.6% te sirovine u suvišku.

Slika 2: Raspodjela sirovina u proizvodu za uvjete definirane početnim slučajem
Figure 2: Distribution of feeds in the product for the initial case requirements



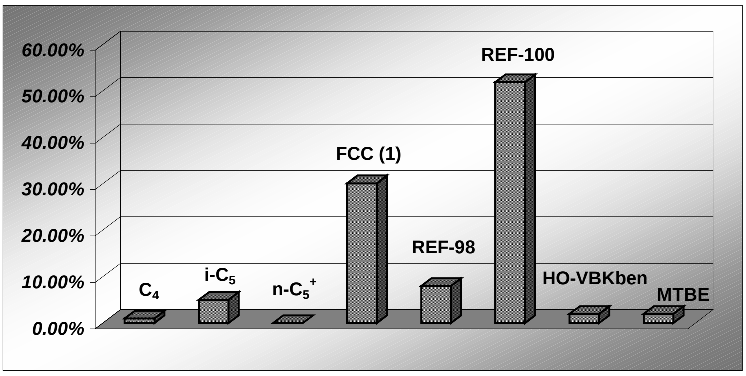
Smanjenjem napona para sa 700 na 600 hPa uz zadržavanje ostalih ograničenja kao u početnom slučaju dobiven je sljedeći optimalni sastav benzina (slučaj 2). Kao što se može vidjeti iz grafičkog prikaza emisija, smanjenjem tlaka para na vrijednost koja odgovara specifikacijama goriva u 2005. g. smanjena je ukupna emisija organskih komponenata za 30%.

Slika 3: Raspodjela sirovina u konačnom proizvodu za uvjete definirane u slučaju 2
Figure 3: Distribution of feeds in the product for the second case requirements



Kako je promjena emisije organskih komponenata kroz ispušne plinove neznatna, smanjenje ukupne VOC emisije je ostvareno smanjenjem emisije zbog emisije hlapljivih organskih tvari (*diurnal losses, hot-soak losses, running losses* i emisije hlapljivih komponenata koje nastaju pri punjenju spremnika vozila). Zbog smanjenja napona para došlo je do gubitka visoko oktanske butan/buten komponente čega je posljedica smanjenje količine proizvedenog benzina (smanjena zarada).

Slika 4: Raspodjela sirovina u konačnom proizvodu za uvjete definirane u slučaju 3
Figure 4: Distribution of feeds in the product for the third case requirements

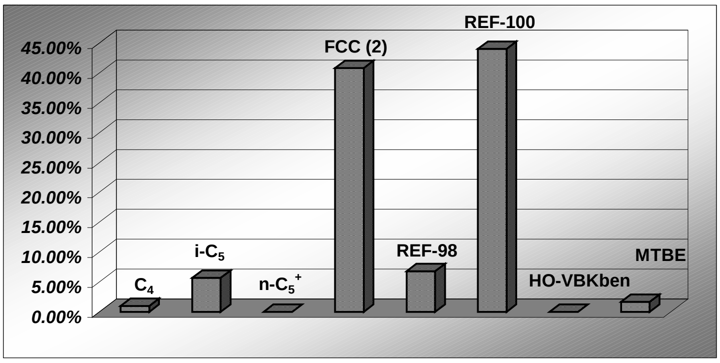


Promjene ostvarene dobiti te ukupne količine namiješanog motornog benzina za svaki razmatrani slučaj prikazane su na slikama 11 i 12. Kao i u prethodnom slučaju, analiza strukture *Dual Price* pokazuje da je umješavanjem dodatne količine visoko oktanskih komponenata moguće ostvariti veći profit. U slučaju 3 količina sumpora je ograničena na 50 ppm dok su ostale specifikacije i ograničenja zadržane.

FCC benzin iz prethodnog slučaja zamijenjen je s hidroobrađenim benzinom čije su specifikacije prikazane u tablici 5. Uspoređujući sastav benzinskog poola s prethodna dva slučaja vidljiv je manji udio FCC benzina za oko 7%, što se može pripisati smanjenju oktanskog broja pri hidroobradi. Smanjenjem udjela FCC benzina pada i ukupna količina namiješanog benzina što uz povećanu cijenu FCC komponente dovodi do sniženja zarade (slika 11). Količina nenamiješanog FCC benzina iznosi 596 t/d ili 44,1%. Hidroobradom FCC benzina pored ciljane desulfurizacije dolazi i do zasićenja olefina koji uvelike doprinose nastajanju dušikovih oksida, uz to olefini su i mnogo reaktivniji pri stvaranju ozona u nižim slojevima atmosfere. Kao što se moglo očekivati, sve promatrane emisije su smanjene, s tim što je smanjenje NO_x emisije dodatno naglašeno smanjenim udjelom olefina u benzinu (u odnosu na prethodni slučaj sadržaj olefina je smanjen za 10%).

Hidrodesulfurizacija FCC sirovine kao tehnološka opcija za smanjenje sadržaja sumpora u benzinu je razmotrena u slučaju 4. Neznatno smanjenje oktanskog broja FCC benzina kao i uklanjanje ograničenja vezanog uz sumpor uvjetovali su povećanje količine namiješanog krekiranog benzina od 10% u odnosu na prethodni slučaj (slika 12). Unatoč višoj cijeni (tablica 5) i nešto nižoj zaradi izraženoj po toni proizvoda zbog daleko veće količine proizvedenog benzina (447 t/d ili 15%) ostvaren je veći profit (slika 11).

Slika 5: Raspodjela sirovina u konačnom proizvodu za uvjete definirane u slučaju 4
Figure 5: Distribution of feeds in the product for the fourth case requirements



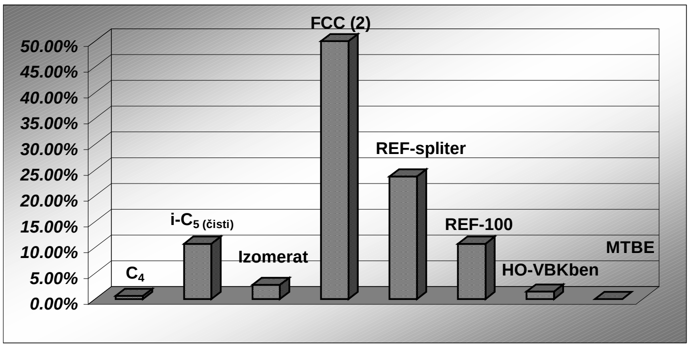
Za razliku od prethodnog slučaja doprinos visokooktanskih komponenata ukupnom profitu je manji, iako ni u ovom slučaju taj doprinos nije zanemariv. Zbog smanjenog sadržaja aromata, benzena i kisika nastavljen je trend pada svih emisija osim emisije dušikovih oksida koja je narasla radi povećanog udjela olefina u proizvodu.

Sljedeći slučaj (slučaj 5) predstavlja daljnje približavanje europskoj kvaliteti goriva predviđenih za 2005. godinu. U benzinski pool uvedene su nove sirovine i to:

- donji produkt splitiranja reforming benzina (teški reformat)
- izomerizat dobiven izomerizacijom depentaniziranog lakog primarnog benzina i produkata hidrogenacije gornjeg produkta splitera
- i-pentan visoke čistoće

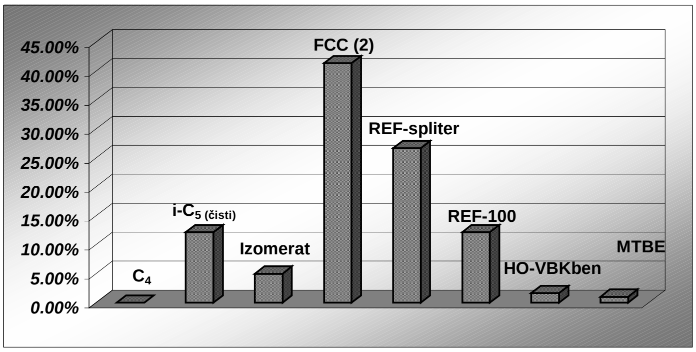
Ograničenja u modelu su zadržana iz prethodnog slučaja osim za aromate (maks. 35%) i benzen (maks. 1%). Optimalna formulacija benzina za promatrani slučaj je prikazana na slici 6, dok su fizikalno-kemijske značajke benzina prikazane u tablici 5. Bitna razlika između ovoga i prethodnih slučajeva je to što je u suvišku teški reformat i MTBE dok su i-pentan i FCC benzin u deficitu tj. količina namiješanog benzina nije ograničena oktanskim brojem.

Slika 6: Raspodjela sirovina u konačnom proizvodu za uvjete definirane u slučaju 5.
Figure 6: Distribution of feeds in the product for the fifth case requirements

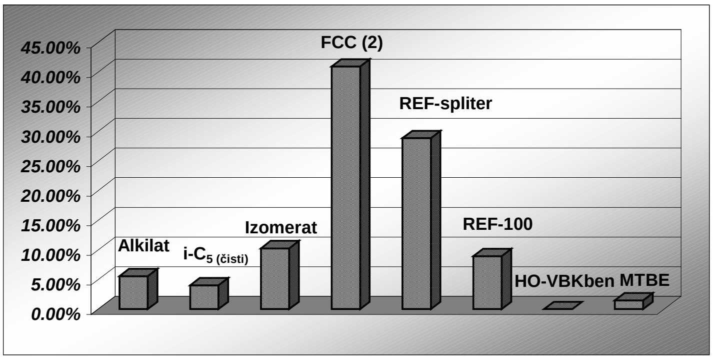


U prilog toj tvrdnji idu i vrijednosti *Dual Pricea* za i-pentan (92,1 $/t) te FCC benzin i hidroobrađeni visbreaking benzin, dok su te vrijednosti za visokooktanske komponente jednake nuli. Pad VOC emisija kao i emisije toksičnih tvari je evidentan zbog smanjenog sadržaja benzena, aromata i kisika dok je porast emisije dušikovih oksida povezan s porastom olefina i sumpora u odnosu na prethodni slučaj.

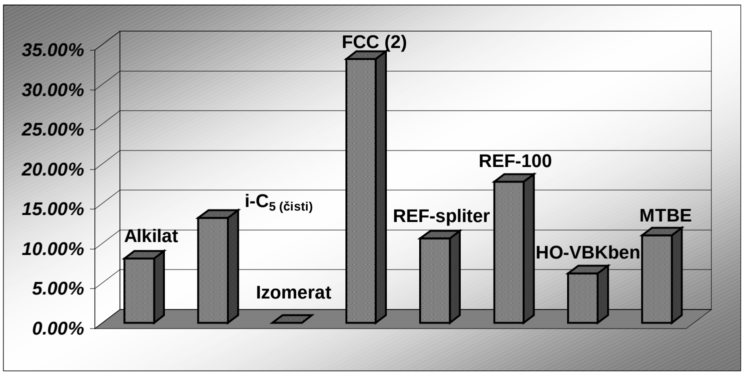
Slika 7: Raspodjela sirovina u konačnom proizvodu za uvjete definirane u slučaju 6
Figure 7: Distribution of feeds in the product for the sixth case requirements



Slika 8: Raspodjela sirovina u konačnom proizvodu za uvjete definirane u slučaj 7
Figure 8: Distribution of feeds in the product for the seventh case requirements

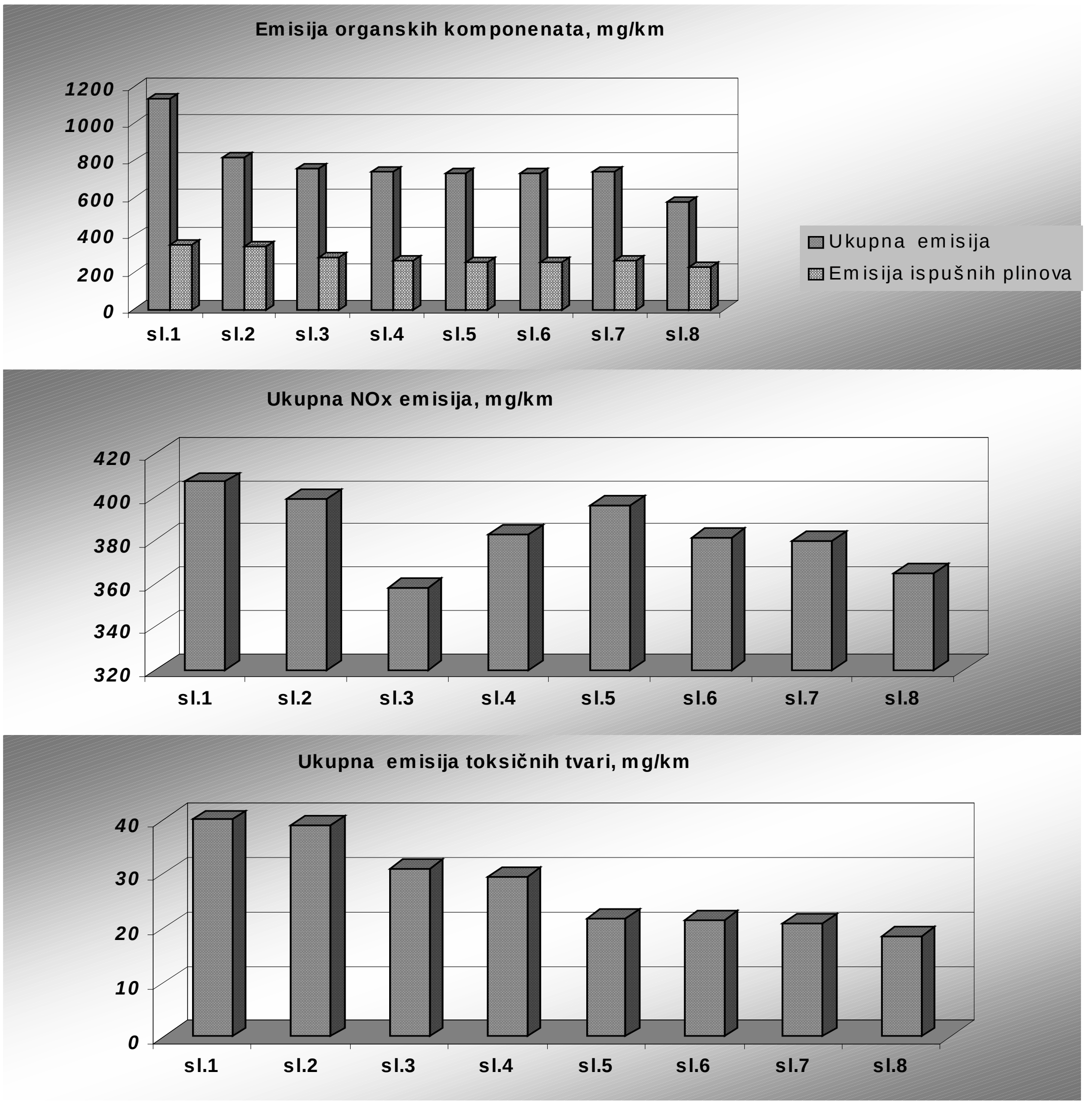


Slika 9: Raspodjela sirovina u konačnom proizvodu za uvjete definirane u slučaju 8
Figure 9: Distribution of feeds in the product for the eighth case requirements



Slika 10: Grafički prikaz promjene organskih komponenti, dušikovih oksida i toksičnih tvari za svaki razmatrani slučaj

Figure 10: Graph of the emission changes of organic components, nytrogen oxides and toxic substances for each case considered



VOC emission, mg/km

sl. = case

Total emission

Exhaust gases emission

Total NO_x emission

Total toxic substances emission

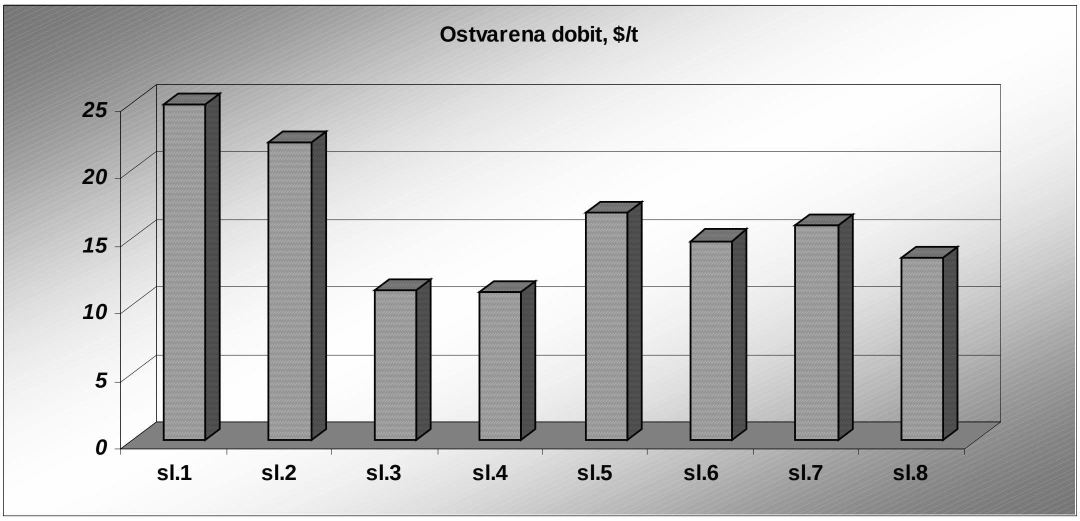
Slučaj 6 je istovjetan prethodnom uz maks. ograničenje sadržaja olefina od 15 vol.%. Tim ograničenjem su potpuno zadovoljene pretpostavljene buduće specifikacije motornih benzina 2005. godine. Radi postavljenog ograničenja za olefine iz benzinskog poola je potpuno uklonjena C_4 frakcija, te je iz istog razloga smanjen udio FCC benzina. Emisije su gotovo ostale nepromjenjene osim NO_x emisije koja je nešto niža u odnosu na predhodni slučaj iz prije navedenih razloga.

Prednosti alkilata kao sirovine za namješavanje motornih benzina su prikazane u slučaju 7. Zbog svog parafinskog karaktera, niskog napona para te visokog oktanskog broja uporaba alkilata posredno valorizira ostale sirovine za namješavanje motornih benzina.

To se najbolje može vidjeti u grafičkom prikazu zarade ($/t) odnosno optimalne količine proizvedenog benzina (slika 11, odnosno slika 12). Posljedni slučaj je optimalna formulacija reformuliranog benzina uz korištenje resursa iz prethodnog slučaja, a prema kriterijima koje je postavila EPA kroz projekt Phase II.

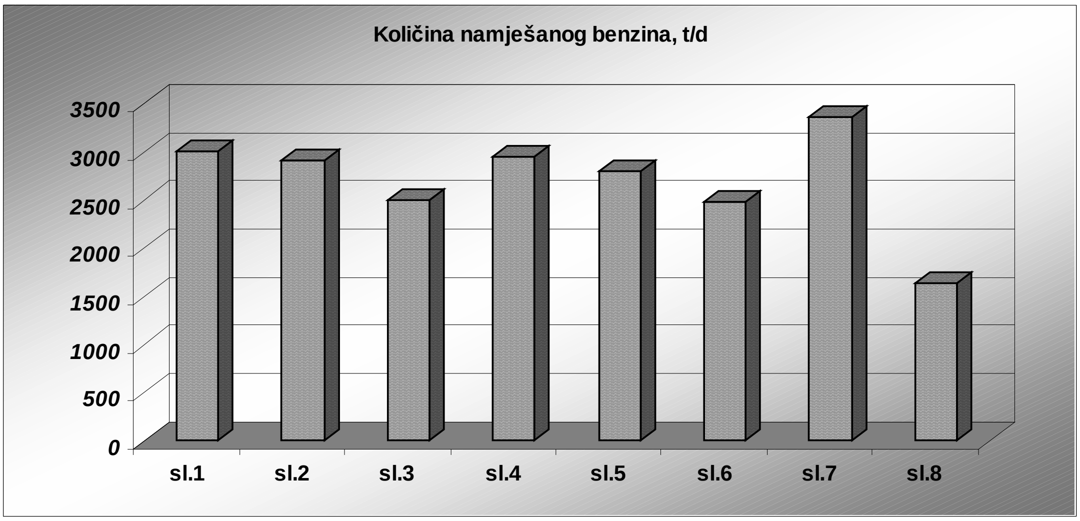
Slika 11: Ostvarena dobit za svaki pojedini slučaj uz navedena ulazna ograničenja LP modela

Figure 11: Profit made in each particular case with indications of the LP model input limitations



Profit raised sl. = case

Slika 12: Optimalna količina motornog benzina koja je dobivena uz navedena ulazna ograničenja LP modela
Figure 12: Motor gasoline optimum quantity obtained with the indicated input limitations of LP Model



Blended gasoline volume sl. = case

Zaključci

Na osnovi opisanih postupaka reformuliranja motornih benzina sukladno budućim zahtjevima kvalitete mogu se donijeti sljedeći zaključci:

- Smanjenje emisije postignuto je prilagodbom ključnih parametara kvalitete benzina budućim zahtjevima kvalitete.
- Tehnološke opcije proizvodnje benzina razmatranih formulacija procijenjene su optimiranjem rafinerijskih procesa i operacija:
  - smanjenja sadržaja sumpora opcijom predobrade FCC sirovine pokazala se boljom prema optimalnim rješenjima, u odnosu na opciju obrade FCC benzina,
  - zadovoljavanje budućih zahtjeva sadržaja benzena u benzinima postignuto je opcijom splitiranja reformata,
  - namješavanjem alkilata kao komponente motornog benzina postignuta je najveća dobit ($/d).

REFORMULATION OF MOTOR GASOLINES ACCORDING TO THE FUTURE QUALITY REQUIREMENTS

Abstract

Auto Oil Programme presented in the middle of 1996 by the European Union Commission determined the allowed emissions from motor vehcles and consequently influenced the future quality of motor fuels. On the basis of comprehensive tests performed within the Programme, there have been defined critical parameters of fuel quality included in the EU Specifications to be applied since 2000 and 2005. The novelty of these Specifications lies in the fact that they determine also the structural group composition of fuels with extremely strict requirements regarding the sulphur content restrictions (limitations).

Due to these limitations, achievement of the main applicational properties of fuels (octane number or cetane number) will require from refineries a careful formulation of fuels, i.e. optimization of composition for the purpose of meeting the strictly prescribed limits of emissions from engines. Limitation of the sulphur content in motor fuels represents an additional factor essentially determining the fuel quality and directing the technological development of refineries. Optimization of motor fuel blending therefore represents an extremely important factor in the fuel production, particularly in case of restricted resources taking into consideration the availability of individual blending components. The objective of optimization is in achieving the quality parameters with an acceptable cost-effectiveness.

This work has dealt with the example of optimal formulation of unleaded motor gasoline. Mathematical model of blending has been formed by the method of linear programming with limitations prescribed by the "Auto Oil Programme".

Introduction

The Auto Oil Program, presented towards the middle of 1996 by the EU Commission, sets the limits of permitted motor vehicle emission and conditions the quality of motor fuels (1,2). Based on the tests conducted in the scope of the Program, key fuel quality parameters have been set, based on which European fuel specifications have been determined. The specifications set qualitative and quantitative structure of the fuel composition, with very stringent requirements referring to sulphur content limitation.

Due to the limitations set, the achievement of principal fuel application properties (octane and cetane number) has faced the refineries with the requirement of formulating fuels, meeting, through their composition, both the specifications and the basic performance requirements. Limitation of sulphur content in motor fuels is an additional factor considerably determining fuel quality and directing technological development of the refineries.

That is why optimization of the motor fuel blending, the purpose of which it is to achieve the set quality parameters with an acceptable cost effectiveness, represents a major factor in fuel production, especially when the resources of individual blending components are limited (3,4,5).

The LP Model

The blending of motor gasoline constitutes a classical problem of finding the optimal goal function that has been set, which may be resolved through the method of Linear Programming. Limitations defined during problem solution refer to the gasoline volumes and specific properties, while the goal function has been determined as profit maximization (6). The LP model used in this paper consists of three mutually connected parts, as may be seen in Figure 1.

We had at our disposal 8 feeds for which it was necessary to set the following: Price ($/bbl, $/t), available volumes (bbl, t), as well as properties: RON, MON, sulphur (mas. %), aromatics (vol. %), olefins (vol. %), benzene (vol. %), oxygen (mas. %), RVP (hPa), density (g/cm^3), characteristic distillation points (E70 ^{0}C, E100 ^{0}C, E180 ^{0}C, E215 ^{0}C)(7)

The model enables the blending of three different motor gasoline types for which it is necessary to enter: Price ($/bbl, $/t), limits of the required volume (bbl, t), as well as specify: minimal RON and MON, maximal volume of sulphur, aromatics, olefins, benzene, and oxygen; and limits within which density, RVP and characteristic distillation points will range (E180 ^{0}C and E215 ^{0}C are limited only by minimal values).

The input of data referring to feeds and products was made through tables written in MS Excel. The programme was created in LINGO software by LINDO Systems Inc, and consists of 27 variables and 390 limitations (8). The software has been conceived in a manner premitting - with some minor modifications – the increase of the number of feeds and products, as well as the introduction of new property and volume limitations.

The results of the solved problem are written in standard LINGO form (*Solution Report*), providing, apart from optimal product function, also the structure of marginal values (*DP-Dual Price*[*]). Apart from that, solutions are also entered into the MS Excel Table from where they may be extracted and used for calculating characteristic product properties. MS Excel permits unlimited use of results obtained.

Emission Calculation

Towards the beginning of the 90s, the Environmental Protection Agency (EPA) has passed a regulation setting fuel quality criteria and the strategy of its further advancement that would guarantee gradual reduction of the tropospheric ozone precursor (smog) emission in nine urban zones across the USA (9,10).

In order to implement such a strategy, a model has been developed, calculating, based on characteristic gasoline properties, the emission of volatile components and exhaust gases. The model consists of 15 non-linear equations obtained by processing the results of a research conducted in the scope of the American Auto /Oil Program**. Motor gasoline was used as referential fuel (Baseline Fuel representing average USA fuel quality for the summer of 1990), the properties of which are shown in Table 1 (11).

The equations describing dependencies between physico-chemical properties and emission may be broken down into the following three groups:

- Seven equations serve for calculating exhaust gas emission, as follows:
- organic components (VOC – Volatile Organic Compounds)

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[*] Dual Price is the value referring to any limitation within the model, while it may be interpreted as the value for which the goal function shall be increased (i.e. decreased, if it is negative) through the increase of the right side of the limitation for the unit value.

** Auto/Oil Air Quality Improvement Research Program

  - nitrogen oxides - NO_x
- toxic substances (benzene, 1,3-butadiene, formaldehyde, acetaldehyde and polyaromatic hydrocarbons)
- Four equations used for the calculation of VOC emission:
- emissions from a vehicle standing still with a cold engine – diurnal losses
- emissions from a vehicle standing still with a warmed up engine – hot-soak losses
- emissions from a moving vehicle – running losses
- VOC emissions generated while filling the vehicle's fuel tank
- Four equations for calculating benzene emission generated at evaporation (benzene emission at evaporation refers to the four aforementioned cases)

Table 3 presents the parameters of these non-linear equations i.e. the impact of gasoline property on individual emission. The model that has been used is based on dependencies given in Table 2. It was elaborated by the Energy Information Administration, U.S. Department of Energy (9,10). The incorporation of the model for emission calculation into the model for the optimal blending of motor gasoline has been made within MS Excel. It is not possible to perform gasoline composition optimization based on limitations constituing the emission calculation model.

The Setting of Initial Case Requirements

The paper has been conceived in such a way that, starting from the valid fuel quality specifications[*], through gradual adaptation of individual properties (RVP, sulphur, benzene, aromatics and olefins), the kind of motor gasoline is formulated that would satisfy European quality in 2005. To this end, 8 UMG-95 formulations have been made, representing, within the limitations set, an optimal composition. A comparison was made of total emission of VOC, VOC emission through exhaust gases, nitrogen oxide emission, and toxic substance emission. Apart from that, a comparison was also made between total profit and total volume of gasoline blended for each particular case.

As the initial case, we have taken the blending feed quality and the gasoline composition obtained as the optimal solution of the refinery LP model for the Rijeka Oil Refinery (12). For the observed case, we have taken two crudes: Iranian Heavy, 63.5% and Brent. The Brent price was taken as $ 26/bbl, from which product prices were derived as well. The volumes of feeds for the blending of motor gasoline were taken with the assumption of using

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[*] Quality set by INA's internal standard

80-90% of processing capacities at the Rijeka Oil Refinery plant, while the volumes and properties of feeds currently not produced were set based on data from bibliography (7,9,13,14). The prices, available volumes, and physico-chemical properties of the blending feeds are shown in Tab. 3 and 4.

The basic limitations disabling the blending of motor gasoline according to future quality requirements refer to sulphur and gasoline. In this sense, the present paper considers several technological options resolving these problems.

Since FCC gasoline contributes the most (even up to 98%) to sulphur share in total gasoline pool, the resolving of the issue of motor gasoline sulphur content means the removal of sulphur from FCC gasoline (15,16).

FCC may be removed from gasoline in one of the following four ways:

- Processing of low-sulphur oil
- Lowering of the FCC gasoline final distillation point
- Subsequent FCC gasoline hydrotreatment
- FCC feed hydrodesulphurization

The first two solutions are short-term and non-cost-effective due to the higher price of low-sulphur crude in the former case, i.e. loss of octanes and blending feed volume in the latter. The present paper considers only the last two cases. According to the data taken over from the refinery LP model for the aforementioned crudes, the FCC feed contains 1.255% of sulphur, resulting in the FCC gasoline sulphur content in the amount of 0.2504 mas.%. Subsequent hydrotreatment of the FCC gasoline is characterized by the octane value lowering, as well as change of other properties, as may be seen from Table 4. The price, as well as the properties of FCC gasoline subjected to a 95% hydrodesulphurization were taken from bibliography (13,14,15,16,17). FCC feed pretreatment, although costlier, has several important advantages with regard to the previous case:

- insignificant lowering of the octane number
- increased FCC process conversion
- in this way, sulphur is removed from all FCC products.

Table 4 provides the price and properties of FCC gasoline obtained through the cracking of hydrodesulphurized feed. Benzene precursors in the gasoline pool are reformate gasoline (around 81%) and FCC gasoline (around 17%). By applying a similar strategy as in sulphur removal, the reformate gasoline benzene content must also be reduced, which may be done in one of the following ways (18):

- Fractionation of the reforming feed (heavy naphtha) by excluding the benzene boiling temperature area
- Lowering the pressure in the reformer
- Reformate splitting and benzene i.e. top splitting product hydrogenation.

The first case requires the lowest expenditures. However, this particular procedure lowers the reforming gasoline octane value. Apart from that, pre-fractioning of the reforming feed cannot satisfy the future motor gasoline benzene content limitation in the maximum amount of 1 vol. %. The second option does not constitute a satisfactory solution either, since it reduces hydrogen generation, conversion, and octane reformate number, while increasing the volume of coke deposited on the catalyst. The present paper considers the option of benzene removal through hydrogenation with previous reformate splitting, after which the saturated products would serve as isomerization feed (UOP's Penex/DIH process).

While optimizing the blending of gasoline meeting the 2005 requirements, alkylate has been used, as a highly valuable feed (Case 7). In the final case, we have shown the optimal formulation of reformulated gasoline in compliance with specifications set within the Phase II[*].

Discussion

The initial case is an optimal formulation of unleaded motor gasoline meeting the existing specifications set by Ina's internal standard. The gasoline composition structure and the generated emissions are shown in Fig. 2 and 10 respectively, while the physico-chemical properties are shown in Table 5.

The minimum octane number value is the basic limitation in the model, as confirmed by high marginal values (Dual Price) of the high octane components (DP_{MTBE} =$ 13.27/, $DP_{REF-100}$ =$ 5.84/bbl). Sulphur limitation down to 990 ppm limits the volume of FCC gasoline, so that 18.6% of that feed appears as surplus.

The lowering of vapour pressure from 700 to 600 hPa while keeping other limitations the same as in the previous case has yielded the following optimal gasoline composition (Case 2). As may be seen from the graphical presentation of emissions, by lowering vapour pressure down to the value matching the 2005 fuel specifications, total VOC emission has been reduced by 30%.

[11*] The reformulated motor gasoline quality set by the EPA's Clean Air Act at force in the USA since 1 January, 2000.

Since the change of VOC emission through exhaust gases is neglectable, the lowering of total VOC emission has been achieved through the lowering of emission due to VOC (diurnal losses, hot-soak losses, running losses, and VOC emission generated while filling vehicle fuel tanks). Due to the lowering of the vapour pressure, there has been a loss of the high octane butane/butene component, resulting in the lowered volume of gasoline produced (reduced profit). The change of the profit raised and of the blended motor gasoline volume for each considered case is shown in Figures 11 and 12. Same as in the previous case, the analysis of the Dual Price structure shows that a higer profit may be raised by blending in an additional quantity of high octane components.

In Case 3, sulphur content is limited to 50 ppm, while other specifications and limitations have been kept.

FCC gasoline from the previous case has been replaced by hydrotreated gasoline whose specifications are shown in Table 5. While comparing the gasoline pool composition with the previous two cases, we may observe that the share of FCC gasoline is lower by around 7%, which may be ascribed to octane number lowering at hydrotreatment. The lowering of the FCC gasoline share reduces also the total volume of the gasoline blended, leading, through the increased cost of the FCC component, to reduced profit (Figure 11). The volume of not blended FCC gasoline amounts to 596 t/d or 44.1%. Hydrotreatment of the FCC gasoline, apart from the targeted desulphurization, leads also to the saturation of olefins largely contributing to the generation of nitrogen oxides. Olefins are also much more reactive when generating ozone in lower parts of the atmosphere. As could have been expected, all the observed emissions have been reduced, with the NO_x emission reduction being furtherly stressed by reduced gasoline olefin content (with regard to the previous case, olefin content has been reduced by 10%).

Hydrodesulphurization of the FCC feed as a technological option for reducing the gasoline sulphur content has been considered in Case 4. A neglectable reduction of the FCC gasoline octane number, as well as the removal of limitation associated with sulphur, have conditioned the increase of the blended cracked gasoline volume by 10 % with regard to the previous case (Figure 12). Despite higher cost (Table 5) and somewhat lower profit expressed per product ton, due to the much larger volume of gasoline produced (447 t/d or 15%), higher profit has been raised (Figure 11).

Unlike the previous case, the contribution of high octane components to total profit is lower, although it is not neglectable in this case either. Due to the lowered content of aromatics, benzene and oxygen, the reduction trend has been continued for all emissions except for that of nitrogen oxides which has increased due to the higher product olefin content.

The next case (Case 5) constitutes further approaching of the European fuel quality envisaged for 2005. New feeds have been introduced into the gasoline pool, as follows:

- reforming gasoline lower splitting product (heavy reformate)
- isomerizate obtained through the isomerization of de-pentanized light naphtha and top splitter hydrogenation products
- high purity i-pentane

Model limitations have been kept from the previous case, except for aromatics (max 35%) and benzene (max 1%). Optimal gasoline formulation for the observed case is shown in Figure 6, while the gasoline physico-chemical properties are shown in Table 5. The important difference between this and the previous cases is that heavy reformate and MTBE are in surplus, while i-pentane and FCC gasoline are defficient i.e. the volume of blended gasoline is not limited by octane number.

This statement is furtherly substantiated by Dual Price values for i-pentane ($ 10.7/bbl), FCC gasoline, and hydrotreated visbreaking gasoline, whereas, when it comes to the high octane components, they equal zero. Reduction of VOC and toxic substances emission is obvious due to reduced content of benzene, aromatics and oxygen, while the increase of nitrogen oxide emission is associated with the increase of olefins and sulphur with regard to the previous case.

Case 6 is the same as the previous one with maximum olefin content limitation in the amount of 15 vol.%. This limitation completely complies with the assumed future (2005) motor gasoline specifications. Due to the limitation set for olefins, the C_4 fraction has been entirely removed from the gasoline pool, while the FCC gasoline share has been reduced for the same reason. The emissions have remained nearly the same, except for NO_x emission, which is somewhat lower with regard to the previous case for the reasons mentioned earlier.

The advantages of alkylate as a feed for blending motor gasoline have been presented in Case 7. Due to its paraffin character, low vapour pressure, and high octane number, the use of alkylates indirectly evaluates other motor gasoline blending feeds.

This is best seen in the graphical presentation of the profit ($/t) i.e. of the optimal volume of gasoline produced (Figures 11 and 12 respectively).

The last case is the optimal formulation of reformulated gasoline, using resources from the previous case, in compliance with criteria set by EPA through the Phase II project.

Conclusions

Based on the motor gasoline reformulation procedures described, in compliance with the future quality requirements, we may make the following conclusions:

- Aimed emission reduction has been achieved through the adjustment of the key gasoline quality parameters to the future quality requirements
- Technological gasoline production options for the formulations considered have been estimated through the optimization of refinery processes and operations:
  - sulphur content reduction through the FCC feed pretreatment option has proven better – in terms of optimal solutions – than the FCC gasoline treatment option
  - compliance with the future gasoline benzene content has been achieved through the reformate splitting option
  - alkylate blending as a motor gasoline component has yielded the highest profit ($/d)

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621.434.019.8 zahtjevi kvalitete motornog benzina	motor gasoline quality requirements
665.6.013 postrojenja i postupci prerade nafte	oil processing plants and technology
65.012.022 linearno programiranje	linear programming
665.613.033 izbor naftnih sirovina, po sastavu	oil feedstock selection on composition
665.6.011 izbor i optimiranje postupaka prerade nafte	oil processing selection and optimizing

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