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PREDNOSTI UPORABE NEOLOVNIH POBOLJŠIVAČA OKTANSKOG BROJA MOTORNIH BENZINA

Sažetak

Sastav motornih goriva je najvažniji faktor koji diktira vrstu i kvalitetu emisije iz vozila. Tlak para benzina, njegov sadržaj benzena, aromata, olefina i kisika te sumpora važni su čimbenici koji utječu na kvalitetu zraka kojeg udišemo. Zabranom uporabe olovnih aditiva, mnogi proizvođači motornih benzina dovedeni su u podređenu poziciju zbog tehnološke zaostalosti. Jedan od načina produljenja preživljavanja je zaustavljanje smanjenja dobiti (profita) koja se očitovala uporabom olovnih aditiva kao poboljšivača oktana.

Uvođenjem MMT (metilciklopentadienil mangan trikarbonil) aditiva na osnovi mangana, rafinerije Hrvatske (INE) čak bi povećale uštedu u odnosu na slučaj uporabe samo olovnih aditiva za proizvodnju motornih benzina. U RN Sisak napravljen je i realiziran plan projekta MMT-proizvodnja BMB. Primjeni MMT (za dodavanje u motorne benzine) prethodila su laboratorijska ispitivanja utjecaja ovog aditiva na benzinske komponente i smjese koje čine kvalitetu komercijalnih motornih benzina.

Namješavanje smjesa slijedilo je recepturu dobivenu na LP modelu. Analitički rezultati potvrdili su korektnost LP modela. Izračun na LP modelu dao je rezultate koji su opravdavali izgradnju instalacije za dodavanje MMT i njegovu primjenu u proizvodnji motornih benzina u RN Sisak. Probni rad od šest mjeseci započeo je 18. listopada 1999., a završio uspješno 18. travnja 2000. Uspoređeni su efekti aditiviranja dobiveni LP modelom s onima u probnom radu.

Uvod

Radi boljeg razumijevanja kompleksnosti cjelokupne problematike postizanja zadovoljavajuće razine oktana motornih benzina potrebno je nešto reći o podjeli motornih benzina i mogućoj proizvodnji i odabiru strategije zadovoljenja potrebnih oktanskih vrijednosti.

Teoretski dio

Podjela motornih benzina po tipu

Motorne benzine dijelimo na:

- Motorne benzine sa dodatkom olovnih aditiva, oznake MB
  - ovi benzini mogu sadržavati (do 2000.) različitu količinu olovnih aditiva (0.15 g Pb/l – 0.5 g Pb/l) ovisno o normama pojedine države,
  - mogu biti različite oktanske razine (86 . . . 98 . .),
  - od 2000. zabranjuje se proizvodnja ovih benzina, s vremenskom odgodom u pojedinim državama.
- Bezolovne motorne benzine, oznake BMB
  - ne sadrže olovo niti olovne aditive
  - mogu biti različite oktanske razine (91 . . . 98 . .).

Proizvodnja motornih benzina

Strategija

1. Unapređenjem tehnološkog procesa
   Za proizvodnju motornih benzina visoke gradacije i bez dodatka aditiva poboljšivača oktana treba raspolagati visokom tehnologijom različitih procesa (alkilacija, izomerizacija).
2. Dodatkom bustera
   Dodatkom bustera (oksigenata) dobivaju se motorni benzini više gradacije jeftinijim načinom, u slučajevima gdje nije tehnologija na dovoljno visokoj razini. Međutim, i njihova se uporaba ograničava.
3. Dodatkom aditiva poboljšivača oktana
   a) Olovni aditivi
      Grupa aditiva poboljšivača oktana su iz niza tzv. "olovnih" aditiva (TML, TEL) različitih fizikalnih smjesa i kemijskih spojeva.
      Zbog svojih negativnih učinaka na okoliš, dopuštena količina olovnih aditiva se smanjuje zakonskim odredbama do konačne zabrane uporabe.

b) Neolovni aditivi

Sve oštrija ograničenja emisije i količine aromata i olova u benzinu usmjerila su pažnju prema novim dodacima za namješavanje motornih benzina, koji poboljšavaju oktansku razinu, te nemaju ograničenje uporabe od raznih svjetskih "zelenih" asocijacija.

Neki su na osnovi mangana, metilciklopentadienil mangan trikarbonil (MMT) različitih oblika s mogućim dodatnim detergentnim antikorozivnim i drugim "kozmetičkim" osobinama.

Elementi za odabir strategije

Cilj svakog proizvođača je proizvesti jedinicu proizvoda sa što nižom cijenom iste razine kvalitete. Tako i proizvođači iz naftne djelatnosti, kao što su rafinerije nafte INE, žele proizvesti kvalitetan proizvod sa što manjim ulaganjima. S obzirom na tehnološka ograničenja instaliranih postrojenja uvjetovana je i strategija proizvodnje motornih benzina. Međutim, ona u INI još nije prepoznatljiva, barem ne na razini autora ovog rada, iako se nameće. Za odabir strategije mogu poslužiti sljedeći elementi (iz primjera SAD i EU):

- za uvođenje BMB postojali su različiti povodi
- bitne su razlike u konfiguracijama rafinerija
- velika je razlika u zahtjevima udjela proizvodnje dizelskih goriva i motornih benzina
- europski pad oktana zbog promjene
  - 95 BMB = 98 premium 0.15 g Pb/l

Oktani u Europi

Navodimo sljedeće razloge koji utječu na proizvodnu strategiju benzinskog (oktanskog) poola u Europi:

- mnoge su rafinerije opremljene
  - kontinuiranim regeneracijskim reformingom
  - izomerizacijom, alkilacijom, MTBE
- proizvođači i marketing su predvidjeli ograničene zahtjeve za BMB regular
- činjenice koje opravdavaju rano uvođenje BMB 98
- sklonost rafinerija više prema ulaganjima nego rješenjima putem aditiva

Budući scenarij u Europi

Zašto MMT? Zbog:

- nedostatka oktana uzorkovanog strogim specifikacijama za sumpor i aromate
- pritiska da se izbjegnu štete (gubici) zbog zabrane olova od 2000.
- povećanog zanimanja za zaštitu protiv udubljenja sjedišta ventila (Valve Seat Recession)

Koristi i značajke uvođenja MMT:

- poboljšanje oktana nižom cijenom
- osiguranje zaštite sjedišta ventila od udubljenja
- pogodnost i dokazanost korištenja u cjevovodu
- uspješno korišten u Europi također kao poboljšivač izgaranja u dizelovim motorima, koji smanjuje emisiju čestica za oko 20%.

Značajke MMT

Sastav

MMT (metilciklopentadienil mangan trikarbonil) je poboljšivač oktana na osnovi mangana i služi u proizvodnji reformuliranih benzina.

Zbog svojih fizikalnih svojstava MMT je najpovoljniji za uporabu u gorivu. Lako je topljiv u benzinu i uglavnom netopljiv u vodi. Ledište mu je –1°C, a vrelište 232°C.

Proizvođač ovog aditiva je ETHYL komercijalno ime je HITEC 3000 i dolazi u još dvije različite smjese s različitim udjelom mangana i mogućnosti primjene kod niskih okolišnih temperatura (-22°C, -29°C). To su HITEC 3062 (-22°C) i HITEC 3046 (-29°C).

Tablica 1: Svojstva komercijalnog MMT (HITEC 3000)
Table 1: Commercial MMT (HITEC 3000) properties

izgled/appearance		tamno narančasta tekućina/dark orange fluid
ugljikovodici/hydrocarbons		sveukupni/total
voda/water	mg/kg	70
mangan	mas%	24.4
gustoća na/density at 20°C	g/ml	1.38
plamište/flash point	°C	96
ledište/freezing point	°C	-1
vrelište/boiling point	°C	232

Istraživanja u SAD

- U komercijalnu uporabu MMT je uveden 1957. kao primarni antidetonator, a korišten je u olovnim benzinima.
- 1970. koristi se u bezolovnim benzinima
- 1978. MMT se koristi u svim bezolovnim benzinima Kanade

Rezultati ispitivanja na automobilima koji su prešli ogromnu kilometražu na benzin s dodatkom MMT mogu se svesti u zaključke:

- MMT je sigurna, ekonomična i korisna komponenta benzina

- uglavnom je zanimljiv kao antidetonator u bezolovnim benzinima
- s olovnim aditivom djeluje sinergistički i dolazi do izražaja zbog rastućih restrikcija olova u benzinu
- dovoljna je koncentracija od 5–12 mg Mn/l (za benzine Hrvatske 18 mg Mn/l).

Prilog 1: Oktanski odziv s MMT po regijama
Supplement 1: Octane response with MMT per regions

REGIJA/REGION	MMT (mg Mn/l)	IOB OSNOVNOG GORIVA BASE FUEL RON	PORAST IOB RON INCREASE
AZIJA ASIA	0	86.4	
	9	88.6	2.2
	18	89.5	3.1
	0	93.5	
	9	94.5	1
	18	95.1	1.6
SREDNJI ISTOK MIDDLE EAST	0	86.4	
	9	88.4	2
	18	89.3	2.9
JUŽNA AMERIKA SOUTH AMERICA	0	88.0	
	9	89.8	1.8
	18	90.7	2.7
	0	94.1	
	9	95.2	1.1
	18	95.8	1.5
SAD USA	0	92.4	
	9	93.2	0.9
	18	93.6	1.3

- 1988. Ethyl uz konzultaciju s Environmental Protection Agency (EPA) i automobilskom industrijom SAD provodi opsežno ispitivanje utjecaja MMT na:
  - emisiju iz automobila
  - sustav kontrole emisije
  - dijelove automobila u direktnom kontaktu s gorivom
  - zdravlje osoblja koje manipulira gorivom
  - performanse s oksigenatima

Bio je to najopsežniji program ispitivanja jednog aditiva za gorivo, koji je ikada provela jedna privatna kompanija. Analiza Ethylovih istraživanja je potvrdila da:

- MMT uzrokuje značajno smanjenje emisije iz ispušnog sustava automobila

- najznačajnije je smanjenje dušikovih oksida
- aditiv ne djeluje štetno na dijelove automobila, kao što su:
  - senzori kisika
  - injektori goriva
  - katalitički konverteri
- nije evidentirano začepljenje katalizatora niti na jednom od ispitnih automobila
- porasla je moć katalitičke konverzije NO_x
- uporaba MMT u reformuliranim benzinima smanjuje količinu visokoreaktivnih ugljikovodika koji tvore ozon, a reaktivnost se smanjuje od 23 do 30% u odnosu na goriva koja ne sadrže MMT
- 1990. je nastavio dodatna istraživanja s tehničkim i istraživačkim rukovodstvom EPA i Section 211 Clean Air Acta
- sva navedena istraživanja, uspoređujući i kontrolu zraka na koncentraciju mangana u velikim gradovima, gdje se koristio MMT (Toronto) i s onim gdje se MMT nikada nije koristio (London) ukazuju da nema nikakve razlike.

Oktanski odziv

Oktanski odziv MMT u komercijalnim benzinima analogan je onom od olovnih antidetonatora u mnogo čemu, uključujući:

- veći je odziv kod nižih koncentracija antidetonatora
- istraživački oktanski broj uglavnom više raste od motornog oktanskog broja
- odziv IOB i MOB mogu se predvidjeti za pojedine benzine
- porast oktanskog broja ovisi o tipu ugljikovodika i viši je za niže oktanske razine
- sumpor ometa oktanski odziv, ali je njegov utjecaj neznatan
- primjenom konc. MMT od 8 mg Mn/l postignut je prosječan porast oktana od 0.9 jedinica za regular (0.5 – 0.6 za premium), tj. postignut je veći IOB za 1.2-1.5, a MOB za 0.4 – 0.6 jedinica

Oksigenati

- primjenom MMT u koncentraciji mangana od 8 mg Mn/l u smjesama s MTBE, ETBE, etanol i smjesi metanol/etanol dobiven je oktanski odziv od prosječno 3.1 za regular i 2.1 za premium benzin
- nakon 13 tjednog skladištenja sve su smjese oksigenata s MMT bile stabilne

MMT i reforming katalizator

Interesantno je pitanje utjecaja mangana iz benzina u slučaju slopiranja i kasnijeg dolaska sa sirovinom u proces reforminga.

Da li će zatrovati katalizator?

- ne postoji takvo iskustvo, već se odgovor osniva na pretpostavkama i zaključuje se:
    - ako se pretpostavi da mangan u tragovima prođe proces hidroobrade, mogao bi vrlo malo, ili gotovo ništa, djelovati deaktivirajuće na katalizator reforminga. Sasvim sigurno ne toliko, koliko bi to mogli tragovi olova ili arsena.

Sigurnost i rukovanje

- MMT je uvršten u otrove B kategorije.

  Toksičan je za ljude, ako se unosi u organizam inhalacijom, gutanjem ili apsorpcijom kroz kožu. Zato zahtijeva oprezno rukovanje. Rafinerije odavno koriste opasne kemikalije. Ključ za sigurno rukovanje opasnim materijalima je:
  - pravilno izvedena i dobro održavana oprema
  - uvježbano osoblje i
  - pravilan odnos osoblja prema kemikalijama

  Ako je to zadovoljeno MMT-om se može sigurno rukovati.

Prilog 2: Određivanje oktanske osjetljivosti motornih benzina RNS na MMT
Supplement 2: Determination of the sisak oil refinery motor gasoline brands' susceptibility to MMT

	R203	R406	R502	R703
IOB porast/RON increase	1.12	1.29	1.69	2.04
MOB porast/MON increase	0.75	0.86	1.28	1.26
IOB/RON	97.25	95.59	94.45	89.47
MOB/MON	85.77	84.25	83.35	81.59
FIA Aromati, v/v %	40.56	38.17	32.07	26.26

Praktički rad

Prethodna ispitivanja u Rafineriji nafte Sisak

Utvrđivanje oktanske osjetljivosti na MMT

Realizaciji aktivnosti po planovima projekta "MMT – proizvodnja BMB" u RNS prethodilo je ispitivanje oktanske osjetljivosti motornih benzina RNS na

MMT, uz suradnju sa predstavnikom proizvođača aditiva, Ethyl, 18. siječanj 1999. Ispitivanja su provedena sa četiri uzorka motornih benzina u "pripremi" za doradu do komercijalne kvalitete. Svaki je uzorak tretiran sa 9, 18 i 36 mg Mn/l sadržanog u aditivu HITEC 3000, za određivanje IOB i MOB standardiziranim metodama ASTM D 2699-97 i ASTM D 2700-97 CR. Za svaki je uzorak učinjena procjena valjanosti individualnog mjerenja. Određivan je sadržaj aromata (FIA) i ostale fizikalno-kemijske osobine po EN 228.

Utvrđeno je:

- 18 mg Mn/l je dovoljna količina u svim ispitivanim uzorcima za postizanje potrebne razine IOB i MOB zahtjevane normom EN 228 i INA N 02-002/98
- povećanje IOB je 1.12 do 2.04 jedinice
- povećanje MOB je 0.75 do 1.26 jedinice
- sadržaj (FIA) aromata v/v % je od 40.56 do 26.26
- postignuta je kvaliteta BMB 91, 95, 98

Realizacija projekta

Podloga za realizaciju projekta

Podloga za realizaciju projekta je odluka direktora RNS od 15.01.1999. kojom je definiran zadatak, imenovan voditelj projekta, te voditelji i članovi stručnih timova za provedbu projekta radnog naziva "MMT-proizvodnja BMB".

Motorna i laboratorijska ispitivanja

Na osnovi plana projekta MMT – proizvodnja BMB kojeg je 22.01.1999. izradio voditelj projekta i radnog zadatka dobivenog od voditelja s osnovnim smjernicama, načinjen je plan motornih i laboratorijskih ispitivanja, te ostali planovi pojedinih faza projekta. Planom motornih i laboratorijskih ispitivanja planirano je analizirati komponente za namješavanje motornih benzina, a na osnovi rezultata analiza na LP modelu dobiti recepturu za namješavanje, zatim namiješati tražene gradacije motornih benzina, analizirati i aditivirati sa 18 mg Mn/l i odrediti im oktanske vrijednosti.

Rezultati ispitivanja prve serije uzoraka korišteni su za "Prvu analizu namješavanja motornih benzina uz dodatak MMT u Rafineriji nafte Sisak" (Izvješće stručnog tima za optimiranje namješavanja LP modelom). Dobiveni su pozitivni pokazatelji primjene MMT-a. Nakon "Prve analize namješavanja motornih benzina uz dodatak MMT u RNS" izrađen je detaljan plan ispitivanja. Njime su utvrđene potrebne količine uzoraka za kompletnu provjeru rezultata dobivenih LP modelom. Iz tog razloga se 24.03.1999. pristupilo ponovnom uzorkovanju.

LP modelom za namješavanje motornih benzina dobivene su recepture za namješavanje rafinerijskih komponenata i MTBE za olovne i bezolovne motorne benzine, sa i bez MMT, po zadanim varijantama. Svojstva smjesa dobivena računskim putem, preko poznatih svojstava komponenata, potvrđena su laboratorijskim analizama realnih smjesa, namiješanih po recepturi LP modela.

Prilog 3: Namješavanje motornih benzina iz osnovnih komponenata
Supplement 3: Blending of motor gasoline brands out of basic components

		VARIJANTA 2.1 A (s/with MMT)				VARIJANTA 2.1 B (bez/without MMT)				2.2 C (s/with MMT)	2.2 D (bez /without MMT)
Zahtjevi Requirements		**MB98 (0.15)**	**BMB 95**	**BMB 98**	**BMB 91**	**MB98 (0.15)**	**BMB 91**	**BMB 95**	**BMB 98**	**BMB 95**	**BMB 95**
		1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
benz.in vrha splitera top splitter	mas%	4.55	6.38	1.86	29.75	3.05	23.78	4.15	7.57	4.8	2.84
FCC benzin	mas%	37.05	48.91	3.18	10.76	40.35	13.80	43.38	4.26	42.90	42.44
Platformat	mas%	57.04	37.26	92.31	59.49	52.31	62.42	43.53	74.32	48.04	48.22
MTBE	mas%	1.36	7.45	2.65	-	4.3	-	8.94	13.85	4.25	6.49
Pb	g/l	0.15	-	-	-	0.15	-	-	-	-	-
Mn	mg/l	18	18	18	18	-	-	-	-	18	-

FIZIKALNO-KEMIJSKE KARAKTERISTIKE SMJESA MOTORNIH BENZINA/ PHYSICO-CHEMICAL PROPERTIES OF MOTOR GASOLINE BLENDS

Zahtjevi Requirements											
OKTANSKI BROJ:											
istraživ. IOB/RON		98.70	97.76	98.58	93.36	98.6	92.50	96.9	98.0	97.74	96.7
motor. MOB/MON		86.83	84.95	87.08	84.19	87.1	83.80	84.9	87.0	84.85	85.26
olovo/lead	g/l	0.15	-	-	-	0.15	-	-	-	-	-
benzen	vol %	2.52	1.69	3.88	2.57	2.22	2.68	1.96	3.00	2.20	2.36
ukupni sumpor total sulphur	mas%	0.015	0.021	0.001	0.006	0.030	0.006	0.030	0.009	0.018	0.020
gustoća na 15ºC density	kg/m^3	750.0	738.6	771.4	730.7	747.2	738.2	741.6	755.8	745.8	748.8
Destilacija: (*)											
destilat do 70ºC	vol %	30.0	35.5	21.4	35.4	30.9	32.9	33.5	26.1	32.3	31.5
destilat do 100ºC	vol %	53.8	60	44.7	67.5	54.9	62.5	58.4	55.1	56.4	55.6
destilat do 180ºC	vol %	97.6	-	96.1	-	98.2	-	-	-	99.0	98.7
kraj/end	ºC	188.5	175.4	196.6	156.0	186.2	164.4	177.6	171.4	183.2	184.5
ostatak/residue	ºC										
tlak para (Reid) vapour pressure	hPa	778	843	637	848	745	815	747	620	787	806
VLI		988	1091.5	786.8	1095.8	961.3	1045.3	981.5	802.7	1013.1	1026.5

(*) računski/calculated

Analiza ekonomičnosti

Provedena analiza ekonomičnosti namješavanja motornih benzina korištenjem MMT kao poboljšivača oktana temeljena je na Planu prerade od 2.2 mil.t/g, odnosno na ukupnoj količini od 638 572 t/g rafinerijskih benzinskih komponenata s realnim svojstvima i s 18 mg Mn/l za varijante:

1. Asortimana dopuštenog do 2002. (s olovom) u Hrvatskoj
2. Asortimana nakon 2002. (bez olova)

U prvoj varijanti, do 2002., "olovnoj", struktura je motornih benzina sastavljena od MB i BMB različitih gradacija, uporabom rafinerijskih komponenata, MTBE, MMT i Pb-aditiva (olovnih aditiva).

U drugoj varijanti, "bezolovnoj", nakon 2002., zastupljeni su samo BMB različitih gradacija dobivenih uporabom rafinerijskih komponenata i aditiva MMT i MTBE, bez Pb-aditiva (olovnih aditiva).

Prilog 4: Prikaz rezultata analize ekonomičnosti proizvodnje motornih benzina uporabom MMT

Supplement 4: presentation of the cost-effectiveness analysis results of producing motor gasoline using MMT

Motorni benzini Motor gasoline brands	DO/BY 2002.	VARIJANTE VERSIONS	POSLIJE/AFTER	2002.
	A 1.1.1	B 1.1.1	C 1.2.	D 1.2.
Količine MB/MG volumes, kT/god				
Primarni benzin/Naphtha višak vrha splitera/top splitter surplus	-	-	-	-
MB/MG 98 (0.15 g Pb/l)	329.472	337.376	-	-
BMB/UMG 95	251.767	251.767	590.772	605.572
BMB/UMG 98	30.212	30.212	23.500	23.500
BMB/UMG 91	31.219	31.218	29.500	29.500
Poboljšivači/Improvers, t/god				
MMT – HiTEC 3000	62.741	-	62.741	-
MTBE	4098	12000	5200	20000
Pb-aditiv	167.619	171.640	-	-
JBRM/UGRM, $/t	59.05	56.78	63.86	58.32
Razlika JBRM uz HiTEC 1 (lj), $/t UGRM difference using HITEC	A-B 2.27		C-D 5.54	
Razlika JBRM uz HiTEC 2 (z), $/t UGRM difference using HITEC	0.05		3.33	
Razlika JBRM uz HiTEC 3 (z+lj), $/t UGRM difference using HITEC	1.26		4.53	

Zaključci ekonomske analize

1. Usporedbom količina i vrijednosti MTBE i MMT-a za namješavanje motornih benzina vidljivo je da korištenje MMT-a za aditiviranje svih komponenata smanjuje potrošnju MTBE, a time i trošak.
   JBRM (jedinična bruto rafinerijska marža) za motorne benzine korištena je kao ekonomski pokazatelj. Razlika JBRM za varijante A i B odnosno C i D, pokazuje moguće uštede pri proizvodnji motornih benzina uz primjenu MMT.
2. JBRM za motorne benzine najveća je pri proizvodnji motornih benzina MB 98 s 0.5 g Pb/l i BMB gdje se samo u bezolovne benzine dodaje MMT. Ovaj zaključak upućuje da treba proizvoditi MB 98 sa 0.5 g Pb/l dok to dopuštaju norme i zahtjevi tržišta.
3. Povećanje JBRM korištenjem MMT-a u "neolovnoj" varijanti, nakon 01.07.2002. iznosi 5.54 $/t, i veće je nego u "olovnoj", s povećanjem od 2.24 $/t (Prilog 4).
4. Ekonomskom analizom načinjena je i prva procjena valjanosti projekta s pozitivnim učincima, kako je navedeno u prethodnoj točci. S obzirom da su sva prethodna ispitivanja i analitički pokazatelji izvanredni, slijedio je nastavak projekta, sukladno nizu procedura zahtjeva 4.4. ISO 9001 "Kontrola projekta".

Provedba primjene MMT

Ova je faza obuhvaćala:
- izradu projektne dokumentacije za instalaciju
- izgradnju instalacije za dodavanje MMT
- izradu radnih uputa
- probni rad

Instalacija za dodavanje MMT

Naziv: Instalacija za istovar i dodavanje MMT u motorne benzine

Lokacija: Čret, Dorada 2, Etilizacija. Projekt instalacije i njegovu realizaciju proveli su djelatnici RN Sisak.

Oprema:
- kontejner, 10.000 l
- vaga (piezo efekt)
- pumpa
- mjerač volumena
- armature
- cjevovodi

- tankvana
- sustav vode i odvodnje

Projektom je definirano:

- skladišni prostor pojedinih motornih benzina
- način dopremanja aditiva
  - AC
  - ŽC

  Preferirano je dopremanje sa ŽC u ISO tankovima od 5 t.
- Upravljanje instalacijom – radne upute

Probna proizvodnja

Uspješno je obavljena probna proizvodnja s osnovnim motornim benzinom za proizvodnju BMB 95 (5 šarži)

1. šarža: IOB = 94.5
MOB = 84.2

a s 18 mg Mn/l dobiveno je

IOB = 96.6 tj. povećanje IOB = 2.1 jedinice
MOB = 85.2 MOB = 1.0 jedinice

Procjena valjanosti

Usporedbom dobivenih rezultata ekonomske analize na osnovi laboratorijskih ispitivanja i učinaka primjene MMT u industrijskoj probnoj proizvodnji potvrđena je valjanost projekta, utvrđena u izvješću Prva analiza namješavanja motornih benzina uz dodatak MMT u Rafineriji nafte Sisak, od 14.04.1999.

Probni rad

Odlukom direktora je 18. listopada 1999. puštena u šestmjesečni probni rad instalacija za dodavanje MMT koji je trajao do 18.04.2000.

U tom razdoblju bilježile su se:

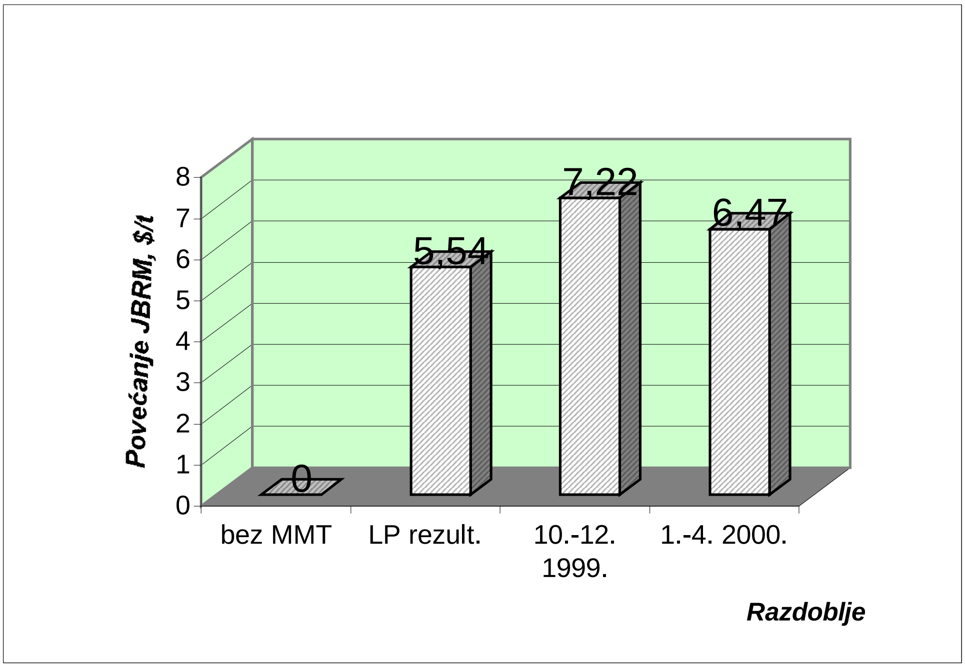
- količine rafinerijskih komponenata i njihovi omjeri namješavanja za određenu kvalitetu motornog benzina
- utrošak MTBE i MMT (HITEC 3062) te
- odziv oktana.

Ekonomski efekti probnog rada

Uspoređena je proizvodnja motornih benzina u RNS za ista razdoblja od šest mjeseci u 1998./99. kada se nije dodavao MMT, s onim u probnom radu primjene MMT. Uočeno je da se primjenom MMT:

- mijenjala struktura motornih benzina u korist prodavanijih gradacija BMB 95 i MB 98 (0.5 g Pb/l)
- Gotovo sav primarni benzin je utrošen za namješavanje u motorne benzine (do 97.7%)
- smanjena je količina uporabe skupog MTBE
- prosječna dobit s MMT po toni benzina iznosila je za studeni i prosinac 1999. 7.22 $/t, a za siječanj-travanj 2000. 6.47 $/t što je više od rezultata dobivenih izračunom na LP modelu (Prilog 5)
- Vrijednost uštede s obzirom na ukupno proizvedene motorne benzine u probnom radu primjene MMT (HITEC 3062) od 18.10.1999. do 18.04.2000. je 1.872.607 $.

Prilog 5: Ekonomski pokazatelji primjene MMT za proizvodnju motornih benzina
Supplement 5: Economic indicators of MMT application for the production of motor gasoline



UGRM increase without MMT LP results Period

Zaključci:

1. Prethodnim ispitivanjima učinkovitosti MMT na oktanske vrijednosti IOB i MOB sa 18 mg Mn/l dale su povećanje

   IOB = 1.12 do 2.04 jedinice

   MOB = 0.75 do 1.26 jedinice

   18 mg Mn/l je optimalna koncentracija za motorne benzine RNS
2. Laboratorijska ispitivanja potvrdila su ispravnost LP modela za davanje receptura namješavanja motornih benzina
3. Ekonomska analiza dala je povećanje JBRM
   - za olovne benzine 2.27 $/t
   - za neolovne benzine 5.54 $/t
4. U probnom radu dobilo se povećanje JBRM 7.22 $/t, što na proizvedenu količinu motornih benzina u 6. mjeseci iznosi 1.872.607 $.
5. Projekt je uspješno i u potpunosti završen i svi postavljeni uvjeti u zadatku su ispunjeni.

ADVANTAGES OF USING UNLEADED MOTOR GASOLINE OCTANE NUMBER IMPROVERS

Abstract

The composition of motor fuels is the most important factor dictating the kind and quality of vehicle emission. Gasoline vapour pressure, as well as its benzene, aromatic, olefin, oxygen and sulphur content, are important factors impacting the quality of air that we are breathing in. Prohibition of using leaded additives has brought many motor gasoline manufacturers into an unfavourable position due to technological outdatedness. One of the ways of prolonging their survival is to stop the reduction of profit manifested through the use of leaded additives as octane improvers.

Through the introduction of MMT (Methylcyclopentadienyl Manganese Tricarbonyl)-a manganese-based additive, Croatian (INA's) refineries would even increase their savings with *respect to using only leaded additives for motor gasoline production. The plan for the project entitled "MMT – UMG Production" has been elaborated and implemented at the Sisak Oil Refinery. The application of MMT for addition into motor gasoline has been preceded by laboratory tests of the said additive's impact on the gasoline components and blends accounting for the quality of commercial motor gasoline.*

The blending of compounds was made according to the formula obtained on the LP model. Analytical results have confirmed the LP model accuracy. Calculation on the LP model has provided results justifying the construction of an MMT addition plant and its application in motor gasoline production at the Sisak Oil Refinery. The 6-month test operation, started on 18 October, 1999, was successfully completed on 18 April, 2000. The LP model addition effects were compared to those obtained during test operation.

Introduction

In order to better understand the complexity of the issue when it comes to achieving a satisfactory motor gasoline octane level, it is necessary to say something about the very classification of motor gasoline brands, their possible production, and the choice of strategy for meeting the required octane values.

The Theoretical Part

Classification of Motor Gasoline Brands per Type

Motor gasoline brands may be classified as follows:

- Motor gasoline with the addition of leaded additives, marked MG
    - this gasoline may (by 2000) contain various quantities of leaded additives (0.15 g Pb/l – 0.5 g Pb/l), depending on individual country's standards
    - it may have different octane levels (86...98...)
    - as of 2000, the production of this gasoline is prohibited, with grace period for some countries.
- Unleaded motor gasoline, marked UMG
    - does not contain lead or leaded additives
    - may have different octane levels (91...98...)

Motor Gasoline Production

Strategy

1. Through technological process advancement
   The production of high grade motor gasoline without octane improver additives requires high technology for various processes (alkylation, isomerization)
2. Through the addition of boosters
   The addition of boosters (oxygenates) yields higher grade motor gasoline in a cheeper way, in cases where technology is not on the sufficient level. However, their use is limited as well.
3. Through the addition of octane improving additives
   a) Leaded additives
      The group of octane improving additives comes from the series of the so called "leaded" additives (TML, TEL), of various physical blends and chemical compounds.
      Due to their negative environmental impact, the permissible quantity of leaded additives is being reduced by legal regulations, until their final phase out.
   b) Leadfree additives
      Growingly stringent emission and gasoline aromatic and lead content limitations have directed the attention towards new additives for the blending of motor gasoline which improve the octane level and the use of which is not limited by the world's "green" associations.
      Some are managenese-based, Methylcyclopentadienyl Manganese Tricarbonyl (MMT), of various forms, with possible additional detergent, anti-corrosion, and other "cosmetic" properties.

Elements for Choosing the Strategy

It is the purpose of every manufacturer to produce a product unit with as low a price as possible, while maintaining the same quality level.

Manufacturers from the oil sector, such as INA oil refineries, also wish to produce a good quality product with as low investments as possible. Given the technological limitations of the plants installed, the strategy of motor gasoline production is also conditioned. However, it is not recognizable yet in INA, at least not in the eyes of the author of this paper, although it is self-evident.

In order to choose the strategy, we may use the following elements:

(based on USA and EU examples)

- there were various motives for the introduction of UMG
- differences in the configuration of refineries are of importance
- there are great differences when it comes to the demand for diesel fuel and motor gasoline production shares
- European octane decrease due to change
  - 95 UMG = 98 premium 0.15 Pb/l

Octanes in Europe

We are citing the following reasons impacting the European gasoline (octane) pool production strategy:

- many refineries are equipped with
  - a continuous regenerative reforming
  - isomerization, alkylation, MTBE
- manufacturers and marketing departments have envisaged limited demand for regular UMG
- the facts justifying an early introduction of UMG 98
- the refineries are more prone to investments then to solutions using additives

The Future European Scenario

Why MMT? Because of:

- lack of octanes caused by stringent sulphur and aromatic specifications
- pressure to avoid losses caused by lead ban as of 2000
- increased interest in protection against valve seat recession

Benefits and properties associated with the introduction of MMT:

- octane improvement at a lower cost
- ensurance of valve seat protection against recession
- proven suitability for use in pipelines
- successfully used in Europe also as combustion improver in diesel engines reducing particulate emission by around 20%

MMT Properties

Composition

MMT (Methylcyclopentadienyl Manganese Tricarbonyl) is a manganese-based octane improver used in the production of reformulated gasoline.

Due to its physical properties, MMT is the most suitable for use in fuel. It is easily gasoline soluble and mostly non-water-soluble. Its freezing point is -1^{0}C, while its boiling point is 232^{0}C.

The additive is produced by ETHYL, and its commercial name is HITEC 3000. It is available in two other different blends, with different manganese shares and the possibility of application at low surrounding temperatures (–22^{0}C, –29^{0}C). They are HITEC 3062 (–22^{0}C), and HITEC 3064 (–29^{0}C).

Research in the USA

- MMT has been introduced into commercial use in 1957 as a primary anti-detonator, used in leaded gasoline.
- as of 1970, it has been used in unleaded gasoline
- as of 1978, MMT has been used in all types of Canadian unleaded gasoline.

Results of tests on automobiles that have covered a huge mileage using gasoline with the addition of MMT may be summarized as follows:

  - MMT is a safe, economical, and useful gasoline component
  - it is mostly interesting as an anti-detonator in unleaded gasoline
  - it has a synergic effect when combined with leaded additive and is gaining in importance due to increasing gasoline lead content restrictions
  - sufficient concentration ranges from 5-12 mg Mn/l (and, for Croatian gasoline brands, 18 mg Mn/l.

- in 1988, in consultation with the Environmental Protection Agency (EPA) and the USA automobile industry, Ethyl conducted a comprehensive research of MMT's impact on:
  - vehicle emission
  - emission control system
  - automobile parts in direct contact with the fuel
  - health of the personnel handling fuel
  - performances with oxygenates

It was the most comprehensive test programme for a fuel additive ever conducted by a private company. The analysis of Ethyl's tests has confirmed that:

- MMT causes a significant reduction of emission from the vehicle's exhaust system
- the most significant reduction is that of nitrogen oxides
- the additive has no negative impact on the automobile parts such as
  - oxygen sensors
  - fuel injectors
  - catalytic converters
- catalyst jamming has not been recorded on any of the test vehicles

- the power of NO_x catalytic conversion has increased
- the use of MMT in reformulated gasoline reduces the volume of highly reactive hydrocarbons generating ozone, while the reactivity is reduced by 23-30% with regard to fuels not containing MMT
- in 1990, additional research was continued with EPA's technical and research managerial staff and in accordance with Section 211 of the Clean Air Act
- all the said research programmes, including the one comparing manganese air concentration in large cities where MMT was used (Toronto) with the one where MMT was never used (London), point that there is no difference whatsoever.

Octane Response

Octane response of MMT in commercial gasoline brands is in many ways analogous to that of leaded anti-detonators, including:

- higher response at lower anti-detonator concnetrations
- research octane number mostly increases more than the motor octane number
- RON and MON response may be predicted for given gasoline brands
- octane number increase is dependent on hydrocarbon type and is higher for lower octane levels
- sulphur impairs the octane response, but its influence is neglectable
- the application of MMT in the concentration of 8 mg Mn/l enables an average octane increase in the amount of 0.9 units for regular (0.5-0.6 for premium) i.e. the RON is higher by 1.2-1.5 units, and MON is higher by 0.4-0.6 units.

Oxygenates

- through the application of MMT in manganese concentration of 8 mg Mn/l in blends with MTBE, ETBE, ethanol, as well as in the methanol/ethanol blend, we have obtained the average octane response of 3.1 for regular and 2.1 for premium gasoline
- after a 13-week storage, all the oxygenate blends with MMT were stable

MMT and Reforming Catalyist

It is interesting to consider the issue of gasoline manganese content impact in case of sloping and subsequent coming, along with the feed, into the reforming process.

Shall it contaminate the catalyst?

- there has been no such experience, but the answer is based on assumptions, and the following is concluded:

- if we assume that manganese in traces passes through the hydrotreatment process, it could have no or just a slight deactivating impact on the reforming catalyst. The impact would never be such as, for instance, that of lead or arsenic traces.

Safety and Handling

- MMT has been classified as a B category poison.

It is toxic for people if introduced into the organism through inhalation, swallowing or absorption through skin. That is why it requires careful handling. Refineries have long used hazardous chemicals. The key for a safe handling of hazardous materials is:

- a proper and well maintained equipment
- trained personnel, and
- a proper relation of the personnel towards the chemicals

If this is met, MMT may be safely handled.

Practical Work

Preliminary Tests at the Sisak Oil Refinery

Establishment of the Octane Susceptibility to MMT

The implementation of the "MMT – UMG Production" project at the Sisak Oil Refinery was preceded by the testing of the Refinery's motor gasoline brands susceptibility to MMT, in co-operation with the additive manufacturer representative (Ethyl, 18 January, 1999).

The tests were performed with four motor gasoline samples under "preparation" for final processing up to commercial quality. Each sample was treated with 9, 18, and 36 mg of Mn/l contained in the HITEC 3000 additive, for determining RON and MON using standardized methods ASTM D 2699-97 and ASTM D 2700-97 CR. Individual measurement validity estimation was made for each sample. Aromatic content (FIA) and other physico-chemical properties were established according to EN 228. The following has been established:

- 18 mg Mn/l is a sufficient quantity to achieve the necessary RON and MON level set by the EN 228 and INA N 02-002/98 standards in all tested samples
- RON increase ranges from 1.12 to 2.04 units
- MON increase ranges from 0.75 to 1.26 units
- aromatic content (FIA) v/v % ranges from 40.56 to 26.26
- the quality of UMG 91, 95, 98 has been achieved

Project Implementation

Project Implementation Basis

Project implementation basis is the Refinery Manager's decision of 15 January, 1999 stating the task and appointing the Project Manager, as well as Heads and members of the Task Forces for implementing the project with the working title of "MMT – UMG Production".

Engine and Laboratory Tests

Based on the plan for the "MMT – UMG Production" project, elaborated by the Project Manager (22 January, 1999), and the task defined by the Heads including basic guidelines, a plan of engine and laboratory tests was made, as well as other plans referring to individual project phases. The plan of engine and laboratory tests included an analysis of the motor gasoline blending components. Analysis on the LP model was supposed to provide the formula for blending, after which the required motor gasoline grades had to be blended, analyzed, added 18 mg Mn/l and ascribed the appropriate octane values.

The test results of the first sample series were used for "The First Analysis of Motor Gasoline Blending with the Addition of MMT at the Refinery" (Report by the Task Force for Blending Optimization Using the LP Model). Positive indicators of MMT application were obtained. After "The First Analysis of Motor Gasoline Blending with the Addition of MMT at the Sisak Oil Refinery", a detailed testing plan was elaborated, setting the necessary sample volumes for a complete check of results obtained by the LP model. That was the reason why another sampling was performed (24 March, 1999).

LP model for the blending of motor gasoline has provided formulas for the blending of refinery components and MTBE for both leaded and unleaded motor gasoline brands, with and without MMT, according to the variants set. The properties of blends were obtained by means of a computer, through the known component properties, and were confirmed by the real blends' laboratory analyses, blended according to the LP model formulas.

Cost-effectiveness Analysis

The cost-effectiveness analysis of blending motor gasoline using MMT as octane improver is based on the Processing Plan of 2.2 mil t/y i.e. on the total quantity of 638,572 t/y of refinery gasoline components with realistic properties and with 18 mg Mn/l for the following variants:

1. Assortment permitted until 2000 (leaded) in Croatia
2. Assortment beyond 2000 (unleaded)

In the first version, until 2000 – the "leaded" one, the structure of motor gasoline brands consists of MGs and UMGs of various grades, through the use of refinery components, MTBE, MMT and lead additives.

In the second version, the "unleaded" one, only UMGs are present, of various grades, obtained through the use of refinery components and MTBE and MMT additives, without lead additives. (Supplement 4)

Economic Analysis Conclusions

1. By comparing the volumes and values of MTBE and MMT for the blending of motor gasoline brands, it may be seen that the use of MMT as additive for all components reduces MTBE consumption and hence also the cost.
   The UGRM (unit gross refinery margin) for motor gasoline was used as the economic indicator. The difference in UGRM for A and B i.e. C and D versions shows possible savings when producing motor gasoline with Octane response with MMT per regions Octane response with MMT per regions the application of MMT.
2. UGRM for motor gasoline is the highest when producing MG 98 motor gasoline with 0.5 g of lead per litre and UMG, when MMT is being added only into unleaded motor gasoline. This conclusion points to the fact that MG with 0.5 g of Pb/l should be produced as long as the standards and the market requirements allow it.
3. Increase of UGRM by using MMT in the unleaded version, beyond 1 July, 2002, amounts to US$ 5.54/t, and is higher than in the leaded one, with an increase in the amount of US$ 2.24/t (Supplement 4)
4. The economic analysis has also accounted for the first project validity evaluation, and with positive effects, as has been said in the previous clause. Given that all the preliminary tests and analytical indicators were outstanding, it was possible to proceed with the project implementation, in compliance with the series of processes under requirement 4.4. of ISO 9001 "Project Control".

"MMT Application Implementation"

This phase encompassed:

- elaboration of project documentation for the plant
- construction of the MMT addition plant
- elaboration of operating instructions
- test operation

MMT Addition Plant

Name: Plant for the unloading and addition of MMT into motor gasoline
Location: Čret, Final Processing 2, Ethylization. The installation project was implemented by the Sisak Oil Refinery employees.

Equipment: container, 10,000 l
scales (piezo effect)
pump
volume measurer
reinforcements
pipelines
storage tanks
water supply and drainage system

The project has identified the following:

- storage space for individual motor gasoline brands
- additive delivery manner
    - road tankers
    - rail tankcars

    Delivery using rail tankcars into 5 t ISO storage tanks is preferred.
- Plant management – operating instructions

Test Production

Test production with the basic motor gasoline for the production of UMG 95 has been successfully performed (5 lots). 1st lot:

RON = 94.5
MON = 84.2

and, with 18 mg Mn/l, we have obtained

RON = 96.6 i.e. RON increase = 2.1 units
MON = 85.2 MON = 1.0 unit

Validity Evaluation

By comparing the economic analysis results based on laboratory tests and effects of applying MMT in industrial test production, the project validity, established in the report "The First Analysis of Motor Gasoline Blending with the Addition of MMT at the Sisak Oil Refinery", of 14 April, 1999, has been confirmed.

Test Operation

Upon the decision by the Manager, on 18 October, 1999, the MMT addition plant was put in the six-month test operation lasting until 18 April, 2000. The following was recorded in the said period:

- volumes of refinery components and their blending ratios for a given motor gasoline quality
- MTBE and MMT (HITEC 3062) consumption, and
- octane response

Economic Effects of the Test Operation

The production of motor gasoline at the Sisak Oil Refinery for the same six-month period in 1998/99, when MMT was not added, was compared with that in the MMT application test operation.

It has been observed that MMT application

- has changed motor gasoline structure in favour of better sold grades UMG 95 and MG 98 (0.5 g of Pb/l)
- nearly all the naphtha was used for blending into motor gasoline (up to 97.7%)
- the volumes used of costly MTBE have been reduced
- average profit per ton of gasoline in November and December of 1999 was US$ 7.22/t, and for January-April, 2000 US$ 6.47/t, which is above the results obtained by calculation on the LP model (Supplement 5)
- The savings achieved given the total volume of motor gasoline produced during the MMT (HITEC 3062) application test operation from 18 October, 1999 to 18 April, 2000 amount to US$ 1 872,607.

Conclusions:

1. Preliminary efficiency tests of MMT with regard to RON and MON octane values with 18 mg Mn/l have provided the increase of

   RON = 1.12 to 2.04 units

   MON = 0.75 to 1.26 units

   18 mg Mn/l is the optimal concentration for the Sisak Oil Refinery motor gasoline brands.
2. Laboratory tests have confirmed the validity of the LP model for providing formulas for motor gasoline blending.
3. Economic analysis has yielded UGRM increase
   - for leaded gasoline, US$ 2.27/t
   - for unleaded gasoline, US$ 5.54/t.
4. Test operation has yielded UGRM increase in the amount of US$ 7.22/t, which, given the amount of motor gasoline produced in 6 months, makes US$ 1 872,607.
5. The project has been successfully completed and all the conditions set in the task have been met.

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