Katica Sertić-Bionda, Tomislav Šarić, Marko Mužic

UTJECAJ PROCESNIH VARIJABLI NA UČINKOVITOST HIDRODESULFURIZACIJE PLINSKOG ULJA

Sažetak

U radu je istražen utjecaj temperature i omjera vodik/ugljikovodici (H_2/CH) u procesu hidrodesulfurizacije vakuum plinskog ulja. Ispitivanja su provedena u eksperimentalnom reaktoru ”Andreas Hofer”, u temperaturnom području od 320 do 380°C, uz promjenjivi omjer H_2/CH od 100 do 300 te uz stalnu prostornu brzinu od $1h^{-1}$ i tlak od 40 bara.

Pokazano je da povećanjem temperature i omjera H_2/CH raste postotak uklonjenog sumpora iz vakuum plinskog ulja. Strukturno-grupnom analizom utvrđeno je povećanje udjela parafinskog ugljika (%C_P) u čitavom temperaturnom području. Nakon početnog smanjenja udjela aromatskog ugljika (%C_A) u odnosu na sirovinu pri nižim temperaturama procesa opaženo je njegovo povećanje s porastom temperature, koje je osobito izraženo pri najvećoj oštrini procesnih uvjeta.

Također su utvrđena smanjenja vrijednosti fizikalnih značajki produkata (gustoća, viskoznost, molekulska masa) s povećanjem temperature i omjera H_2/CH u ispitanom području njihovih vrijednosti.

1. UVOD

Proizvodnja naftnih goriva zadovoljavajućih ekoloških značajki nužno je povezana uz potrebu poboljšanja postojećih procesa prerade nafte, kao i uz odgovarajuća istraživanja na kojima će ona biti temeljena. Spomenuta istraživanja prvenstveno trebaju obuhvatiti utjecaje značajki sirovina i katalizatora, kao i relevantnih procesnih varijabli na prinose i sastav produkata istraživanog procesa[1]. U ovom kontekstu proces dehidrodesulfurizacije ima posebnu važnost s obzirom na njegovu moguću primjenu u smislu poboljšanja značajki sirovina i produkata procesa koji su temeljni

u proizvodnji naftnih goriva [2-6]. Ovo proizlazi iz osnovne uloge procesa hidroobrade koja je usmjerena na uklanjanje sumpora, dušika, aromata kao i drugih nepoželjnih spojeva iz naftnih frakcija. Osim zaštite katalizatora u procesima gdje sumporni i dušikovi spojevi djeluju kao katalitički otrovi, hidrodesulfurizacija ima ulogu poboljšanja kakvoće produkata sa stajališta kemijske stabilnosti, boje, mirisa, cetanskog broja i drugih značajki [7-16]. Primjena ovog procesa nužna je u proizvodnji naftnih goriva koja će zadovoljavati tražene ekološke zahtjeve, prvenstveno vezane uz sadržaj sumpora i aromatskih ugljikovodika. U tom smislu od posebne je važnosti obrada sirovina i/ili produkata procesa katalitičkog krekiranja (FCC), koji doprinosi ukupnom sadržaju sumpora u motornim benzinima čak do 98%, iz čega proizlazi da su navedeni parametri kakvoće naftnih goriva u izravnoj povezanosti s ovim procesom [17-26].

Stoga su u radu utvrđeni utjecaji temperature i omjera H_2/CH pri stalnim vrijednostima ostalih parametara procesa hidrodesulfurizacije plinskog ulja, s ciljem daljnjeg ispitivanja odabranih uzoraka kao sirovina u procesu katalitičkog krekiranja.

2. EKSPERIMENTALNI DIO

2.1. Sirovina i katalizator

Ispitivanja su provedena s vakuum plinskim uljem kao sirovinom, primjenom odgovarajućeg katalizatora za proces hidrodesulfurizacije. Značajke sirovine i katalizatora prikazane su u tablici 1, a uvjeti testiranja u tablici 2.

2.2. Metode

Hidrodesulfurizacija je provedena u visokotlačnom laboratorijskom uređaju, tvrtke Andreas Hoffer, Hochdrucktechnik GmbH, Mülheim-Ruhr, prikazanom na slici 1.

Fizikalne značajke ispitivanih sirovina i uzoraka određene su standardnim metodama: gustoća (ASTM D 1298), viskoznost (ASTM D 445), točka tečenja (ASTM D 97), indeks refrakcije (ASTM D 1218), molekulska masa (ASTM D 2502).

Kemijske značajke određivane su na automatskom analizatoru LECO CHNS-932 za određivanje sadržaja ugljika i vodika, dok je sadržaj sumpora određen na METOREX X-MET 920 (x-ray) fluorescentnom spektrometru.

2.2.1. Opis procesa

Plinsko ulje se kontrolirano dozira pumpom iz dozirne posude i miješa s vodikom neposredno na ulazu u reaktor. U reaktoru se plinsko ulje i vodik zagrijavaju na radnu temperaturu pod radnim tlakom i prolaze kroz sloj katalizatora, gdje se odvijaju reakcije. Nakon reaktora hidroobrađeni produkt hladi se vodom u prethladilu i hladilu. Nakon hladila kondenzirani hidroobrađeni produkt odlazi u visokotlačni odjeljivač gdje se izdvaja plin koji se sastoji od neproreagiranog vodika te manjih količina sumporovodika, smjesa ugljikovodika i amonijaka te drugih plinova i para. Tekući produkt se periodično ispušta u niskotlačni odjeljivač gdje se izvodi ispiranje argonom na povišenoj temperaturi. Ispiranjem argonom na povišenoj temperaturi uklanjaju se zaostali plinovi u produktu i niskohlapljive komponente. Nakon ispiranja

gotovi produkt hidroobrade ispušta se u prihvatnu posudu stripiranog produkta, a plinoviti produkti posebnim cjevovodom odvode u atmosferu.

Tablica 1: Fizikalno kemijske značajke sirovine i katalizatora
Table 1. Phisico-chemical characteristics of feedstock and catalyst

Sirovina		Katalizator - prvi sloj	
gustoća (15°C) , gcm^{-3}	0.8818	Oblik čestica	Kuglice
°API	29.0	Promjer, mm	2-4
viskoznost (40°C) , mm^{2}s^{-1}	14.53	Površina, m^{2}g^{-1}	140
viskoznost (100°C) , mm^{2}s^{-1}	3.29	Volumen pora, cm^{3}g^{-1}	0.4
Točka tečenja, °C	+30	Nasipna gustoća, kgdm^{-3}	0.88
Indeks loma, n$_D^{20}$	1.4938	CoO, mas.%	3.1
Rel. masa	352	MoO, mas.%	12.4
C, %	85.93	**drugi sloj**	
H, %	12.25	Oblik čestica	Cilindrični ekstrudati
S, %	0.99	Promjer, mm	1.2
n-d-M analiza		NiO, mas.%	3.3
% C$_A$	19.34	MoO, mas.%	16.5
%C$_R$	31.65	Volumen pora, cm^{3}g^{-1}	0.42
%C$_N$	12.31	Nasipna gustoća, kgdm^{-}	0.82
%C$_P$	68.35	Lom na tlak, MPa	1.49
R$_A$	0.84		
R$_T$	1.36		
R$_N$	0.52		

2.2.2. Aparati za izvedbu eksperimenta

Plinsko ulje je obrađeno u visokotlačnom laboratorijskom uređaju tvrtke Andreas Hoffer, Hochdrucktechnik GMBH, Mülheim – Ruhr uređaj se sastoji od:

1. pumpe za doziranje smjese za hidroobradu
2. cijevnog reaktora
3. prethladila
4. zmijolikog hladila
5. visokotlačnog odjeljivača
6. sekcije za stripiranje obrađene smjese za hidroobradu

Reaktor

Reaktor (volumen 500 cm^3) je izveden za maksimalni radni tlak od 350 bara i temperaturu do 600°C. U reaktoru je 60 cm^3 katalizatora raspoređenog u 2 sloja (gornji sloj katalizator za hidrodesulfurizaciju, a donji sloj katalizator za hidrodenitrifikaciju), a ispred i iza sloja katalizatora nalazi se sloj keramičkih kuglica (ravnomjerna distribucija sirovine).

Na gornjoj i donjoj prirubnici nalazi se cijev za smještaj termočlanaka, koji registriraju temperaturu. Sigurnosni ventil i manometar cjelokupnog sustava nalazi se na gornjem dijelu reaktora.

Slika 1: Shematski prikaz uređaja za hidrodesulfurizaciju
Figure 1: Schematic presentation of the hydrodesulfurization device
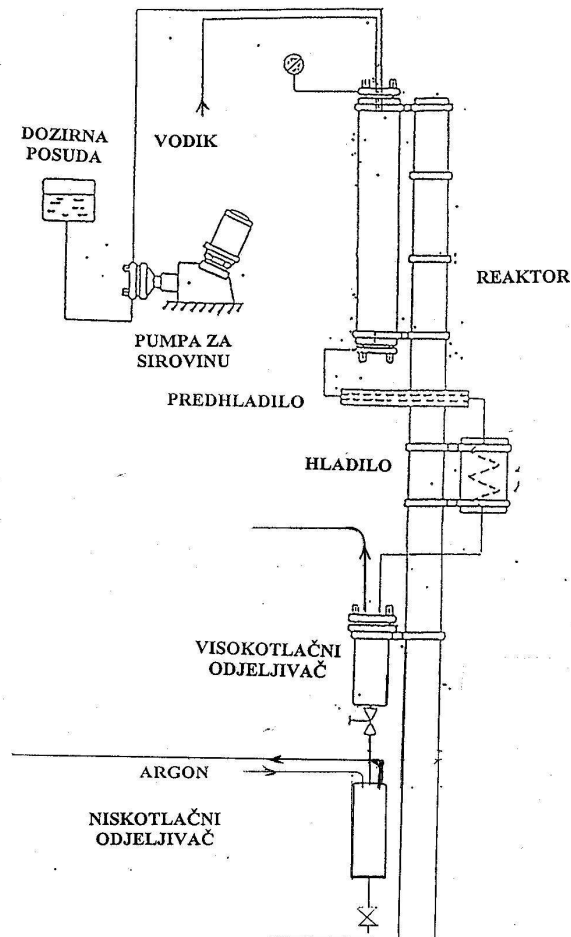
Charging vessel, Hydrogen, Feed pump, Reactor, Precooler,
Cooler, Highpressure separator, Lowpressure separartor

2.2.3. Procesni uvjeti

Uz pomjenjive vrijednost temperature i omjera H_2 / CH (tablica 2), pokusi su provedeni pri uvjetima stalne prostorne brzine od $1h^{-1}$ te tlaka od 40 bara.

Tablica 2: Procesni uvjeti izvedbe eksperimenta
Table 2: Process conditions of experiment performance

T , °C	H_2 / CH	$v(H_2)$, mlmin^{-1}
320	100	200
320	200	400
320	300	600
340	100	200
340	200	400
340	300	600
360	100	200
360	200	400
360	300	600
380	100	200
380	200	400
380	300	600

3. REZULTATI I RASPRAVA

U procesu hidrodesulfurizacije odvija se veći broj reakcija, među kojima su najznačajnije i za proces poželjne reakcije hidrogenolize C-S veze. Njima se stvaraju zasićeni ugljikovodici, uz sumporovodik, koji se odvaja u frakciji plina. U uvjetima industrijske primjene također se zbivaju reakcije cijepanja C-C veza, odnosno hidrokrekiranja, kojima se stvaraju ugljikovodične strukture manje molekulske mase. Reakcije poznate pod nazivom hidrodenitrifikacija uvjetuju stvaranje amonijaka uz odgovarajuću molekulu parafina. Također se odvija hidrogenacija nezasićenih spojeva, što podrazumijeva konverziju olefina u parafine, kao i aromata u naftene. Moguće su i reakcije izomerizacije parafina i naftena, kao i toplinsko krekiranje pri relativno visokim temperaturama. Visoke temperature i sniženi tlakovi povoljno utječu na dehidrogenaciju naftena, kao i na dehidrociklizaciju parafina u aromate.

Zastupljenost pojedinih reakcija u procesu ovisna je o primijenjenom katalizatoru kao i o izboru procesnih parametara. Temeljni parametri, kao što su temperatura, tlak, prostorna brzina i omjer vodik/sirovina (H_2/CH), predmet su optimiranja u odnosu na željenu kvalitetu, kao i ekonomsku bilancu procesa.

U radu su praćeni utjecaji temperature i omjera H_2/CH na stupanj hidrodesulfurizacije, kao i na fizikalno-kemijske značajke dobivenih produkata.

Poznato je da povećanje temperature utječe na povećanje brzina reakcija u procesu, uvjetujući tako povećanje stupnja desulfurizacije. Pri tom se smatra da su reakcije na temperaturama ispod 280°C prespore, a t emperatura od oko 400°C predstavlja na neki način gornju granicu, iznad koje se povećava vjerojatnost prenaglašenog hidrokrekiranja.

S druge strane, omjer H_2/CH, pri konstantnoj temperaturi, tlaku i prostornoj brzini ima utjecaj na isparavanje ugljikovodične smjese, na parcijalni tlak vodika, kao i na vrijeme zadržavanja. S povećanjem omjera H_2/CH, povećava se frakcija isparenog u smjesi, kao i parcijalni tlak vodika, ali se vrijeme zadržavanja smanjuje. Prva dva čimbenika očigledno pozitivno utječu na stupanj desulfurizacije, dok posljednji ima obrnuti učinak. Sve ovo upućuje na složenost djelovanja ovog parametra u procesu. Uz to, važno je istaknuti da omjer H_2/CH ima ključni utjecaj na proces deaktivacije katalizatora, a njegove gornje granice u velikoj su mjeri određene ukupnom ekonomskom bilancom procesa.

Tablica 3: Kemijske značajke hidrodesulfuriziranih uzoraka (uvjeti iz tablice 2)
Table 3: Chemical properties of hydrodesulfurized samples (conditions from Table 2)

T , °C	H_2 / CH	C , %	H , %	S , ppm
320	100	86.31	12.64	3600
	200	86.24	12.61	2500
	300	86.26	12.72	2400
340	100	86.25	12.71	1600
	200	86.31	12.80	934
	300	86.29	12.72	899
360	100	86.44	12.35	555
	200	86.50	12.87	514
	300	86.46	12.82	460
380	100	86.46	12.80	398
	200	86.57	12.83	280
	300	86.44	12.86	248

Ispitivanja su provedena s vakuum plinskim uljem kao sirovinom, čije su fizikalno-kemijske značajke prikazane u tablici 1. Tijekom procesa praćene su promjene gustoće, viskoznosti, točke tečenja, indeksa refrakcije i molekulske mase u odnosu na početnu sirovinu, kao i na utjecaj procesnih parametara. Kemijske promjene

utvrđene su primjenom n-d-M metode, kao najčešće korištene metode za strukturno grupnu analizu. Strukturno grupni podaci (%C_A, %C_N, %C_R, %C_P) izračunati su primjenom empirijskih jednadžbi, a na temelju eksperimentalno određenih veličina; indeksa refrakcije, gustoće i molekulske mase. U zadanom temperaturnom području (320 - 380°C) i pri različitim omjerima H_2/CH (100 - 300), praćene su promjene sadržaja sumpora u produktima procesa hidrodesulfurizacije.

Iz dobivenih rezultata (tablica 3, slika 2), vidljivo je smanjenje sadržaja sumpora u produktu s povećanjem temperature, kao i omjera H_2/CH. Pri najvećoj oštrini procesnih parametara, tj. temperaturi od 380^0C i omjeru H_2/CH od 300 postignuto je smanjenje sumpora od 97,5% u odnosu na njegov sadržaj u početnoj sirovini. Dobiveni rezultati u suglasju su s literaturnim podacima, kao i s općenito potvrđenim utjecajima procesnih parametara na stupanj hidrodesulfurizacije [25].

Slika 2: Ovisnost sadržaja sumpora o temperaturi i omjeru H_2/CH (uvjeti iz tablice 2)
Figure 2: Sulfur content dependence on temperature and H_2/CH ratio (con. from T.2)
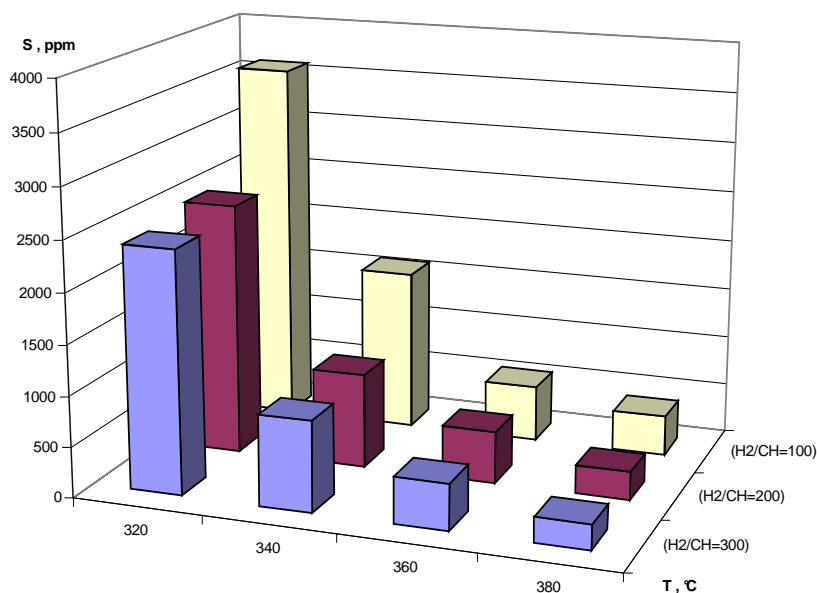
Kako je već rečeno, u radu su praćene i promjene kemijskog sastava produkata primjenom strukturno grupnih podataka, dobivenih n-d-M metodom. Spomenuta metoda se uobičajeno koristi za rutinske analize težih frakcija, kao što su vakuum plinska ulja. Međutim treba napomenuti da njezina primjenjivost ima ograničenja s obzirom na područje ugljikovodičnih i neugljikovodičnih struktura, prisutnih u

ispitivanom uzorku. Ovu činjenicu treba uzeti u obzir kod tumačenja vrlo malih promjena u strukturno grupnom sastavu, koje su zabilježene porastom temperature i omjera H_2/CH. Također, treba istaknuti da su rezultati ove analize prihvatljivi kao pokazatelji trenda, a ne kao apsolutne vrijednosti.

Rezultati n-d-M analize pokazuju lagano povećanje postotka aromatskog i parafinskog ugljika (%C_A i %C_P), kao i smanjenje postotka naftenskog i cikličkog ugljika (%C_N i %C_R), s porastom temperature (tablica 4, slike 3-5).

Tablica 4: Strukturno-grupne značajke hidrodesulfuriziranih uzoraka (uvjeti iz tab. 2)
Table 4: Structural-group properties of hydrodesulfurized samples (condit. from T. 2)

| Omjer H_2/CH Ratio H_2/CH	T, °C	320	340	360	380
100	%C_A	17.17	18.70	19.24	20.53
	%C_R	30.44	30.37	30.43	29.03
	%C_N	13.27	11.67	11.19	8.50
	%C_P	69.56	69.63	69.57	70.97
	R_A	0.74	0.79	0.81	0.83
	R_T	1.43	1.28	1.29	1.19
	R_N	0.69	0.49	0.48	0.36
200	%C_A	17.91	18.74	19.36	20.94
	%C_R	29.62	29.56	28.43	28.40
	%C_N	11.71	10.82	9.07	7.46
	%C_P	70.38	70.44	71.57	71.60
	R_A	0.77	0.79	0.81	0.85
	R_T	1.37	1.25	1.20	1.16
	R_N	0.60	0.46	0.39	0.31
300	%C_A	17.35	19.50	19.31	21.00
	%C_R	28.62	28.09	28.19	27.25
	%C_N	11.27	8.59	8.88	6.25
	%C_P	71.38	71.91	71.81	72.75
	R_A	0.77	0.83	0.73	0.86
	R_T	1.37	1.20	1.22	0.50
	R_N	0.60	0.37	0.39	0.27

Slika 3: Ovisnost sadržaja parafinskog ugljika o temp. i omjeru H_2/CH (uvjeti iz tab.2)
Figure 3: Dependence of paraffinic carbon content on temp. and H_2/CH ratio (cond. from T. 2)
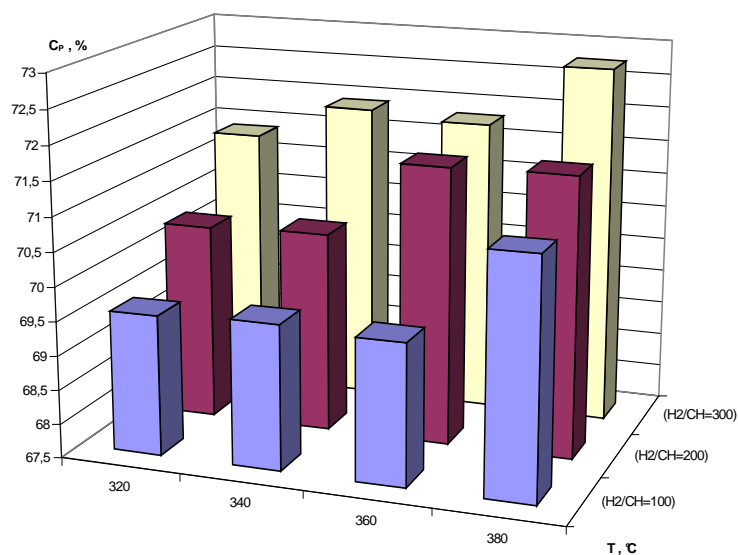
Slika 4: Ovisnost sadržaja aromatskog ugljika o temperaturi i omjeru H_2/CH (uvjeti iz tablice 2)
Figure 4: Dependence of aromatic carbon content on temp. and H_2/CH ratio (cond. from T. 2)
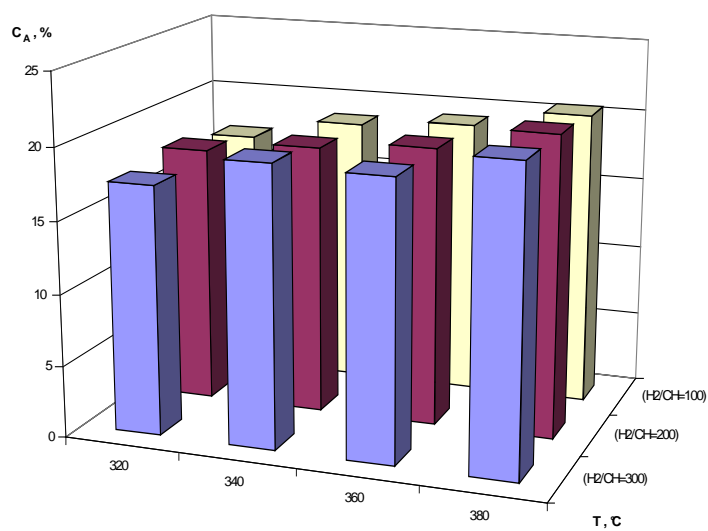
Slika 5: Ovisnost sadržaja naftenskog ugljika o temperaturi i omjeru H_2/CH (uvjeti iz tablice 2)
Figure 5: Dependence of naphthenic carbon content on temp. and H_2/CH ratio cond. from T.2)
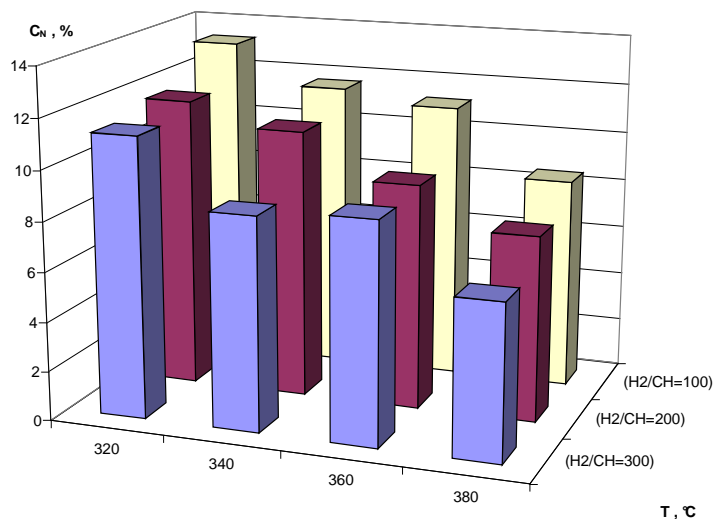
Povećanje postotka parafinskog ugljika (%C_P), vidljivo na slici 3, zbiva se na račun hidrogenacije ugljikovodika olefinskog tipa, koji se pojavljuju kao intermedijeri u reakcijama hidrodesulfurizacije, što je često povezano s krekiranjem cikličkih struktura. Spomenute reakcije krekiranja uvjetuju smanjnje postotka naftenskog (%C_N) i cikličnog (%C_R) ugljika, a naglašenije su pri većoj oštrini procesnih parametara, tj. višoj temperaturi i omjeru H_2/CH (tablica 4, slika 5)

Iz ovisnosti postotka aromatskog ugljika (%C_A) o temperaturi, vidljivo je njegovo smanjenje s obzirom na postotni udjel u sirovini, što ukazuje na odvijanje reakcija hidrogenacije aromatskih struktura. Međutim, s porastom temperature zbivaju se mali pomaci u smjeru povećanja postotka aromatskog ugljika, koji su dosta izraženi pri temperaturi od 380°C. Tako je udjel aromatskog ugljika u sirovini smanjen od 19,34% na 17,35% pri temperaturi od 320°C i omjeru H_2/HC od 300, dok pri maksimalnoj temperaturi od 380°C uz isti omjer H_2/HC on doseže vrijednost od 21,00%. Očigledno, ova temperatura, u kombinaciji s ostalim procesnim parametrima, inhibira reakcije hidrogenacije aromata, koje su općenito naglašene u uvjetima nižih temperatura i viših tlakova. Iz toga proizlazi da je hidrogenaciju aromata u naftene moguće pospješiti izborom višeg tlaka u procesu, što u konkretnom slučaju znači primjenom tlaka iznad 40 bara.

Mehanizmi odvijanja reakcija hidrodesulfurizacije izučavani su na primjerima različitih ugljikovodika, a rezultati istraživanja na spojevima tiofenske skupine

pokazali su da hidrogenacija aromatskih prstena nije nužna za hidrogenolizu C-S veza u aromatskim strukturama. Tako reakcijska shema za dibenzotiofen pokazuje veću brzinu reakcije izdvajanja sumporovodika iz ugljikovodične strukture, nego što je to slučaj za reakcijski mehanizam koji uključuje parcijalnu hidrogenaciju aromata[7].

Ova istraživanja mogu poslužiti u tumačenju dobivenih rezultata, prema kojima sadržaj izdvojenog sumpora nije u povezanosti sa stupnjem hidrogenacije aromatskih struktura (slike 2 i 4).

Tijekom eksperimentalnog rada praćene su i promjene temeljnih fizikalnih značajki produkata hidrodesulfurizacije. Osim točke tečenja, za sva ispitana fizikalna svojstva (gustoća, viskoznost, indeks refrakcije, molekulska masa), postignuta su smanjenja njihovih vrijednosti, i s obzirom na sirovinu i s povećanjem temperature i omjera H_2/CH (tablica 5, slike 6 i 7).

Tablica 5: Fizikalne značajke hidrodesulfuriziranih uzoraka (uvjeti iz tablice 2)
Table 5.Phisical properties of hydrodesulfurized samples (conditions from Table 2)

Omjer H_2/HC	T ,°C	320	340	360	380
100	Gustoća (20°C), gcm^{-3}	0.8698	0.8656	0.8659	0.8643
	Viskoznost (40°C),mm^{2}s^{-1}	14.76	13.65	12.59	10.08
	Viskoznost (100°C),mm^{2}s^{-1}	3.38	3.21	3.06	2.76
	Točka tečenja,°C	30	30	30	30
	Indeks loma, n_D^{20}	1.4887	1.4882	1.4888	1.4890
	Relativna masa	350	342	340	328
200	Gustoća (20°C), gcm^{-3}	0.8686	0.8644	0.8636	0.8640
	Viskoznost (40°C), mm^{2}s^{-1}	14.32	13.30	12.60	10.36
	Viskoznost (100°C), mm^{2}s^{-1}	3.33	3.17	3.05	2.80
	Točka tečenja, °C	30	30	30	30
	Indeks loma, n_D^{20}	1.4890	1.4878	1.4880	1.4892
	Relativna masa	348	342	340	326
300	Gustoća (20°C), gcm^{-3}	0.8677	0.8643	0.8643	0.8637
	Viskoznost (40°C), mm^{2}s^{-1}	14.62	13.80	12.71	10.90
	Viskoznost (100°C), mm^{2}s^{-1}	3.39	3.25	3.14	2.88
	Točka tečenja, °C	30	30	30	30
	Indeks loma, n_D^{20}	1.4883	1.4885	1.4884	1.4893
	Relativna masa	360	344	346	332

Slika 6: Ovisnost viskoznosti o temperaturi i omjeru H_2/CH (uvjeti iz tablice 2)
Figure 6: Dependence of viscosity on temperature and H_2/CH ratio (cond. from Table 2)
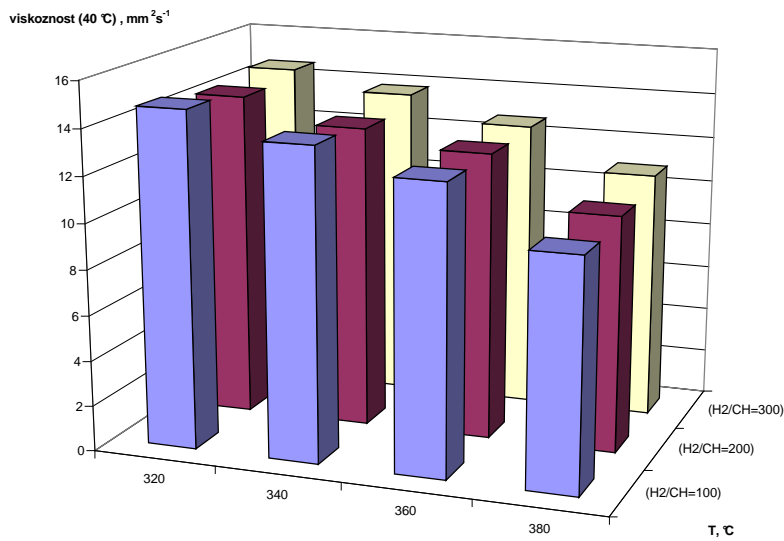
Slika 7: Ovisnost gustoće o temperaturi i omjeru H_2/CH (uvjeti iz tablice 2)
Figure 7: Dependence of density on temperature and H_2/CH ratio (cond. from Tab.2)
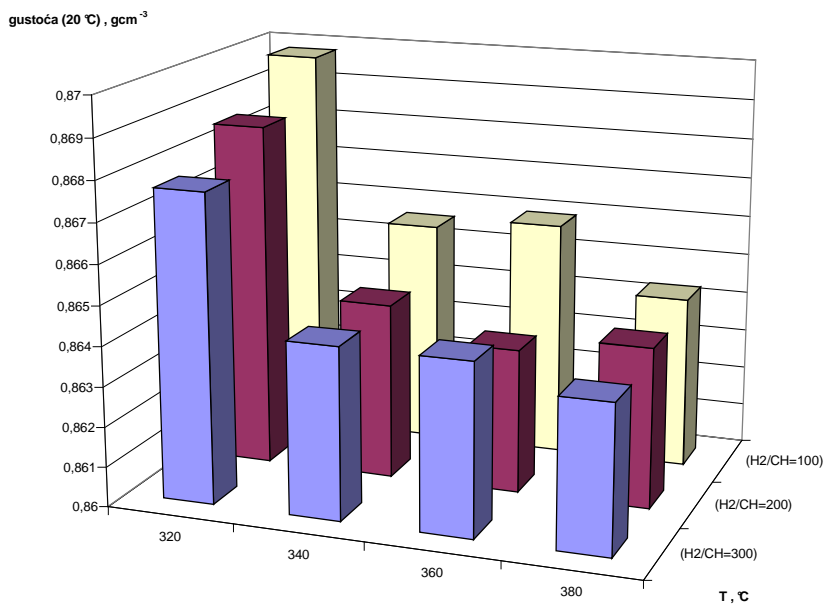
4. ZAKLJUČAK

U radu je ispitan utjecaj temperature i omjera H_2/CH u procesu hidrodesulfurizacije na kemijske i strukturne promjene sastava plinskog ulja, posebice sa stajališta smanjenja sadržaja sumpora i aromatskih ugljikovodika. Na osnovi eksperimentalnih rezultata i provedene rasprave izvedeni su sljedeći zaključci:

- Povećanje oštrine procesnih uvjeta, temperature u području od od 320°C do380°C te omjera H_2/CH od 100 do 300, povoljno je utjecalo na stupanj hidrodesulfurizacije. Pri maksimalnoj oštrini procesa, temperaturi od 380°C i omjeru H_2/CH od 300, postignuto je smanjenje od 97,5% sumpora s obzirom na njegov sadržaj u sirovini.

- Kemijske promjene, praćene n-d-M metodom, pokazale su povećanje udjela parafinskog ugljika (%C_P), uz istodobno smanjenje udjela naftenskog (%C_N) i cikličkog (%C_R) ugljika.

- Smanjenje udjela aromatskog ugljika (%C_A) u produktima, u odnosu na primijenjenu sirovinu, opaženo je pri nižim temperaturama procesa, što se može tumačiti egzotermnošću reakcija hidrogenacije aromata.

- Povećanje udjela aromatskog ugljika pri višim temperaturama procesa, posebice pri temperaturi od 380°C (%C_A=21,00 za omjer 300) u vezi je s povoljnim utjecajem temperature na endotermne reakcije dehidrogenacije naftena, kojima nastaju aromati.

- Neslaganje postotka izdvojenog sumpora sa stupnjem hidrogenacije aromata, s promjenom procesnih uvjeta, može se objasniti činjenicom da hidrogenoliza C-S veza ne mora biti u nužnoj povezanosti s hidrogenacijom aromatskih struktura.

- Praćene analize fizikalnih značajki produkata (gustoća, viskoznost, indeks refrakcije, molekulska masa) pokazale su očekivana smanjenja vrijednosti ovih svojstava s povećanjem oštrine procesnih uvjeta.

THE EFFECT OF PROCESS VARIABLES ON THE EFFICIENCY OF GAS OIL HYDRODESULFURIZATION

Abstract

The paper investigates the effect of temperature and hydrogen/hydrocarbons (H$_2$/CH) ratio in the hydrodesulfurization process of vacuum gas oil. The tests have been performed at the experimental reactor "Andreas Hofer", within the temperature range from 320 to 380°C, with a variable H$_2$/CH ratio from 100 to 300; with a constant space velocity of 1h^{-1} and a 40 bar pressure.

It has been shown that the increase of temperature and H$_2$/CH ratio is followed by the increase of sulphur removed from the vacuum gas oil. The structural-group analysis has shown the increase of the paraffinic carbon share (%C$_P$) in the entire temperature range. After the initial reduction in the aromatic carbon share (%C$_A$) with regard to the feed, at lower process temperatures, we have noticed its increase with the increase of temperature, particularly pronounced at the highest severity of process conditions.

Also established have been reductions in the value of the products' physical properties (density, viscosity, molecular mass), with the increase of temperature and H$_2$/CH ratio within the tested area of their values.

1. INTRODUCTION

The production of petroleum fuels with satisfactory environmental properties is inevitably associated with the need of improving the existing oil processing units, as well as with the necessary research on which the actual improvements shall be based. The research in question must encompass primarily the impact of feed and catalyst properties, as well as that of the relevant process variables, on the yield and composition of the researched proces products[1]. In this sense, the dehydrodesulfurization process has a special significance, given its possible application in the sense of improving the properties of both the feeds and the process products, being fundamental in the production of petroleum fuels [2-6]. This results from the basic role of the hydrotreatment process, directed towards removing sulphur, nitrogen, aromatics, as well as other unwanted compounds, from the oil fractions. Apart from protecting the catalyst in the processes where sulphur and nitrogen compounds act as catalytic poisons, hydrodesulfurization has the role of improving the quality of products from the viewpoint of chemical stability, colour,

odour, cetane number and other properties [7-16]. The application of this process is necessary in the production of petroleum fuels that will meet the required environmental criteria, associated primarily with the content of sulphur and aromatic hydrocarbons. In this sense, of particular importance is the treatment of feeds and/or products of the fluid catalytic cracking process (FCC). Its contribution to the total sulphur content in motor gasoline is up to 98%, which means that the said petroleum fuels quality parameters are directly associated with the process in question [17-26].

That is why the present paper defines the impacts of temperature and H_2/CH ratio at constant values of other parameters on the gas oil hydrodesulfurization process, with the purpose of furtherly testing selected samples as feeds in the catalytic cracking process.

2. THE EXPERIMENTAL PART

2.1. The Feed and the Catalyst

Tests have been performed using vacuum gas oil as feed, by applying the appropriate catalyst for the hidrodesulfurization process. Feed and catalyst properties are shown in Table 1, while the testing conditions are shown in Table 2.

Table 1: The physico-chemical properties of feed and catalyst

Feed		Catalyst - first layer	
density(15°C), gcm^{-3}	0.8818	Particle form	Balls
API / °API	29.0	Diameter, mm	2-4
viscosity(40°C), mm^2s^{-1}	14.53	Surface, m^2g^{-1}	140
viscosity(100°C), mm^2s^{-1}	3.29	Pore volume, cm^3g^{-1}	0.4
Pour point, °C	+30	Bulk density, $kgdm^{-3}$	0.88
Refractive index, n_D^{20}	1.4938	CoO, wt.%	3.1
Rel. M_n	352	MoO, wt.%	12.4
C, %	85.93	second layer	
H, %	12.25	Particle form	Cylindric extrudates
S, %	0.99	Diameter, mm	1.2
n-d-M analysis		NiO, wt.%	3.3
% C_A	19.34	MoO, wt.%	16.5
%C_R	31.65	Pore volume, cm^3g^{-1}	0.42
%C_N	12.31	Bulk density, $kgdm^{-3}$	0.82
%C_P	68.35	Breaking Pressure, MPa	1.49
R_A	0.84		
R_T	1.36		
R_N	0.52		

2.2. The Methods

Hydrodesulfurization has been performed at the high pressure laboratory device manufactured by the "Andreas Hoffer" company, Hochdrucktechnik GMBH, Mülheim-Ruhr, shown in Figure 1.

The physical properties of tested feeds and samples have been determined using standard methods: density (ASTM D 1298), viscosity (ASTM D 445), pour point (ASTM D 97), refractive index (ASTM D 1218), molecular mass (ASTM D 2502).

The chemical properties have been determined on the automatic analyzer LECO CHNS-932 for determining carbon and hydrogen content, while the sulfur content was determined using the METOREX X-MET 920 (x-ray) fluorescent spectrometer.

2.2.1. The Process Description

Gas oil is being carefully dosed using the pump from the dosage vessel and mixed with hydrogen at the immediate reactor entrance. At the reactor, gas oil and hydrogen are being heated up to the operating temperature under operating pressure and pass through the catalyst layer, where the reactions proceed. After the reactor, the hydrotreated product is being cooled using water in the pre-cooling and cooling section. After that, the condensed hydrotreated product goes to the high pressure separator, where gas is being separated. Thus separated gas consists of hydrogen that has not undergone the reaction and smaller volumes of hydrogen sulphide, compounds of hydrocarbons and ammonia, and other gases and vapours. The liquid product is periodically released into the low pressure separator where it is rinsed using argon at an increased temperature. Argon rinsing at an increased temperature removes the left over gases in the product, as well as low volatility components. After the rinsing, the finished hydrotreatment product is released into the reception vessel of the stripped product, while the gaseous products are released into the atmosphere, using a special pipeline.

2.2.2. The Equipment for Conducting the Experiment

Gas oil has been treated in the high pressure laboratory device manufactured by the "Andreas Hoffer" company, Hochdrucktechnik GmbH, Mülheim-Ruhr. The device consists of:

1. pump for dosing the hydrotreatment blend
2. pipe reactor
3. pre-cooler
4. serpentine cooler
5. high pressure separator
6. section for stripping the hydrotreatment blend

The Reactor

The reactor (volume: 500 cm^3) has been performed for maximum operating pressure of 350 bar and temperature up to 600°C. The reactor has 60 cm^3 of catalyst distributed in 2 layers (top layer: catalyst for hydrodesulfurization and bottom layer:

catalyst for hydrodenitrification), while in front of and behind the catalyst layer, there is the layer of ceramic balls (for an even distribution of the blend).

The upper and lower edge have a pipe with thermo cells, registering temperature. The safety valve and manometer of the entire system are in the upper part of the reactor.

2.2.3. The Process Conditions

The hydrotreatment procedures have been performed under conditions listed in Table 2.

3. RESULTS AND DISCUSSION

The hydrodesulfurization process involves a number of reactions, the most significant ones, as well as the most wanted for the process, being the C-S bond hydrogenolysis reactions. They generate saturated hydrocarbons, with hydrogen sulphide, being separated in the gas fraction. Under conditions of industrial application, there are also the reactions of C-C bonds cracking i.e. hydrocracking, generating hydrocarbon structures with low molecular mass. The reactions known as hydrodenitrification condition ammonia generation, with a proper paraffin molecule. There is also the hydrogenation of unsaturated compounds, implying the conversion of olefins into paraffins, as well as that of aromatics into u naphthenes. Possible are also the reactions of isomerization of paraffins and naphthenes, as well as thermal cracking at relatively high temperatures. High temperatures and lowered pressures have a favourable impact on the dehydrogenation of naphthenes, as well as on the dehydrocycling of paraffins into aromatics.

The representation of individual reactions in the process is dependent on the catalyst applied, as well as on the choice of process parameters. The basic parameters, such as temperature, pressure, space velocity and hydrogen/feed (H_2/CH) ratio are the object of optimization with regard to desired quality, as well as to the economic process balance.

The paper monitors the impact of temperature and H_2/CH ratio on the hydrodesulfurization degree, as well as on the physico-chemical properties of obtained products.

It is known that temperature increase has an impact on increasing the velocity of reactions in the process, thus conditioning the increase of the desulfurization degree. In this sense, reactions on temperatures below 280℃ are considered as too slow, while the temperature of around 400℃ constit utes in a way the upper limit above which the probability of a too pronounced hydrocracking appears.

On the other hand, the H_2/CH ratio at constant temperature, pressure and space velocity has an impact on the evaporation of the hydrocarbon blend, the partial hydrogen pressure, as well as on the time of stay. With the increase of the H_2/CH ratio, the evaporated fraction in the blend also increases, as well as partial hydrogen pressure, but the time of stay is reduced. The first two factors obviously have a

positive impact on the desulfurization degree, while the latter has an opposite effect. All this points to the complexity of this particular parameter's activity in the process. Apart from that, it is important to point out that the H_2/CH ratio has a key impact on the catalyst deactivation process, while its upper limits are to a large extent conditioned by the overall economic balance of the process.

The tests were performed using vacuum gas oil as feed. Its physico-chemical properties are shown in Table 1. Monitored during the process were the changes in density, viscosity, pour point, refractive index and molecular mass with regard to the initial feed, as well as to the impact of process parameters. The chemical changes were identified using the n-d-M method, as the one used most frequently for structural-group analysis. The structural-group data (%C_A, %C_N, %C_R, %C_P) were calculated using empirical equations, based on experimentally determined values; refractive index, density and molecular mass. Within the given temperature area (320 - 380°C) and at various H_2/CH ratios (100 - 300), monitored were the changes of sulfur content in the hydrodesulfurization process products.

From the results obtained (Table 3, Figure 2), one may observe reduction of sulfur content in the product with temperature increase, as well as that of the H_2/CH ratio. At the highest severity of process parameters, i.e. temperature of 380^0C and H_2/CH ratio of 300, sulfur reduction of 97.5% with regard to its content in the initial feed has been achieved.

The obtained results are consistent with data from the references, as well as with confirmed impacts of process parameters on hidrodesulfurization degree in general[25].

As we have already mentioned, the present paper monitors also the changes in the chemical composition of products by the application of structural-group data obtained using the n-d-M method. The said method is usually used for routine analyses of heavier fractions, such as vacuum gas oils. However, we should point out that its applicability has limitations given the area of hydrocarbon and non-hydrocarbon structures present in the sample tested. This fact should be taken into account when interpreting very slight changes in the structural-group composition, recorded through temperature and H_2/CH ratio increase.

The results of n-d-M analysis show a slight increase in the percentage of aromatic and paraffinic carbon (%C_A i %C_P), well as reduction in the percentage of naphthenic and carbon rings(%C_N i %C_R), with temperature increase, (Table 4, Figures 3-5).

Increase in the percentage of paraffinic carbon (%C_P), presented in Figure 3, happens at the expense of hydrogenation of hydrocarbons of olefinic type, appearing as intermediaries in hydrodesulfurization reactions, which is often connected with the cracking of ring structures. The said cracking reactions condition reduction in the percentage of naphthenic (%C_N) and carbon rings (%C_R), while they are the most pronounced at a higher severity of process parameters, i. e. higher temperature and H_2/CH ratio (Table 4, Figure 5).

From the dependence of the aromatic carbon percentage (%C_A) on temperature, one may observe its reduction with regard to the percentage share in the feed, pointing to hydrogenation reactions of aromatic structures. However, temperature increase is accompanied by slight changes towards increasing the percentage of aromatic carbon, which are quite pronounced at the temperature of 380°C. Thus the share of aromatic carbon in the feed is reduced from 19.34% to 17.35% at the temperature of 320°C and a H_2/HC ratio of 300, while, at the maximum temperature of 380°C and the same H_2/HC ratio, it reaches the value of 21.00%. Obviously. this temperature, combined with other process parameters, inhibits hydrogenation reactions of aromatics, which are otherwise pronounced under conditions of lower temperatures and higher pressures. This means that the hydrogenation of aromatics into naphthenes may be encouraged by choosing higher pressure in the process, which in this particular case means by applying pressure over 40 bar.

Table 5: Physical properties of hydrodesulfurized samples (conditions from Table 2)

H_2/HC ratio	T,°C	320	340	360	380
100	Density (20°C), gcm^{-3}	0.8698	0.8656	0.8659	0.8643
	Viscosity (40°C), mm^2s^{-1}	14.76	13.65	12.59	10.08
	Viscosity (100°C), mm^2s^{-1}	3.38	3.21	3.06	2.76
	Pour point ,°C	30	30	30	30
	Refractive index, n_D^{20}	1.4887	1.4882	1.4888	1.4890
	Relative mass M_n	350	342	340	328
200	Density(20°C), gcm^{-3}	0.8686	0.8644	0.8636	0.8640
	Viscosity (40°C), mm^2s^{-1}	14.32	13.30	12.60	10.36
	Viscosity (100°C), mm^2s^{-1}	3.33	3.17	3.05	2.80
	Pour point , °C	30	30	30	30
	Refractive Index, n_D^{20}	1.4890	1.4878	1.4880	1.4892
	Relative mass M_n	348	342	340	326
300	Density (20°C), gcm^{-3}	0.8677	0.8643	0.8643	0.8637
	Viscosity (40°C), mm^2s^{-1}	14.62	13.80	12.71	10.90
	Viscosity (100°C), mm^2s^{-1}	3.39	3.25	3.14	2.88
	Pour point, °C	30	30	30	30
	Refractive Index, n_D^{20}	1.4883	1.4885	1.4884	1.4893
	Relative mass M_n	360	344	346	332

The mechanisms of hydrodesulfurization reactions were studied on examples of various hydrocarbons, while the results of research on the compounds of tiofenic group have shown that the hydrogenation of aromatic rings is not necessary for the hydrogenolysis of C-S bonds in aromatic structures. Thus the reaction outline for dibenzotiofene shows a higher speed of reaction of hydrogen sulfide isolation from the hydrocarbon structure than is the case for the reaction mechanism involving partial hydrogenation of aromatics [7].

This research may be of use in the interpretation of the obtained results according to which the content of isolated sulfur is not associated with the hydrogenation degree of aromatic structures (Figures 2 and 4).

During experimental work monitored also were the changes in basic physical properties of hydrodesulfurization products. Apart from the pour point, all other tested physical properties (density, viscosity, refractive index, molecular mass), have achieved a reduction in value, both with regard to feed, and with regard to temperature and H_2/CH ratio increase (Table 5, Figures 6 and 7).

4. CONCLUSION

The paper investigated the effect of temperature and H_2/CH ratio in the hydrodesulfurization process on the chemical and structural changes in the composition of gas oil, particularly from the viewpoint of reducing the content of sulfur and aromatic hydrocarbons. Based on experimental results and the discussion that followed, the following conclusions were drawn:

- Increase in the severity of process conditions: temperature in the area of 320°C to 380°C and H_2/CH ratio from 100 to 300, has had a favourable impact on hydrodesulfurization degree. At maximum process severity: temperature of 380°C and H_2/CH ratio of 300, a 97.5% sulfur reduction has been achieved with regard to its content in the feed.

- Chemical changes, monitored using the n-d-M method, have shown an increased share of paraffinic carbon ($\%C_P$), with a simultaneous reduction in the share of naphthenic ($\%C_N$) and carbon rings ($\%C_R$).

- Reduction in the share of aromatic carbon ($\%C_A$) in the products, with regard to the feed applied, has been observed at lower process temperatures, which may be explained by the exothermal character of aromatic hydrogenation reactions.

- Increased share of aromatic carbon at higher process temperatures, especially at the temperature of 380°C ($\%C_A=21,00$ for a 300 ratio) is associated with the favourable impact of temperature on endothermal reactions of naphthene dehydrogenation, generating aromatics.

- Lack of co-ordination between the percentage of isolated sulfur and the aromatic hydrogenation degree, with the change in process conditions, may be explained

by the fact that the hydrogenolysis of C-S bonds need not necessarily be associated with the hydrogenation of aromatic structures.

- Performed analyses of the products' physical properties (density, viscosity, refractive index, molecular mass) have shown an expected reduction in the value of these properties with the increase of process conditions.

5. Literatura/ References:

1. F. E. Bingham, P. Christensen, Revamping HDS Units to Meet High Quality Diesel Specifications, Asian Pacific Refining Tehnology Conference, Kuala Lumpur,2000.
2. Kinley, J. B.: The Hydrodesulfurization of liquid petroleum fractions, Catalyisis,Vol. 5., Reinhold, New York, 1957.
3. I. Maček, Primjena pogonskih materijala, Tehnički školski centar, Zagreb, 1978.
4. J. C. Guibet, E. Faure-Birchem, *Fuels and Engines*, Editions Technip, Paris, 1999.
5. McKetta, J. J.: Petroleum Handbook, Marcel Dekker Inc., New York, 1992.
6. Bland, W. F., Davison, R. L.: Petroleum Processing Handbook, McGrow-Hill, New York, 1967.
7. Gates, B. C., Katzer, J. R., Schuit, G. L. A.: Chemistry of Catalytic Processes, McGrow-Hill, New York, 1979.
8. G. F. Froment, B. Delmon, P. Grange, Proceedings of the 1st International Symposium/6th European Workshop, Oostende, Belgium, 1997, Elsevier Amsterdam 1997.
9. Tomson, C. J., et. al.: Sulphur compound characterization Studies on High-Boilng Petroleum Fractions, Am. Chem. Soc., Div. Petrol. Chem., Symposium, Pittsburgh, 1966.
10. Durshel, H. V., et. al.: Isolation and Characterization of Sulfur Compound in High-boilng Petroleum Fractions, Anlytical Chem., **39** (1967) 1819-1829.
11. Suyder, F. L. R.: Am. Chem. Soc., Div. Petrol. Chem., Prep. **4**(2) (1970) C 43.
12. Brandenburg, C. F., Latham, D. R.: J. Chem. Eng. Dat., **13** (1968) 391.
13. Quader, D. R., Hill, D. R.: Ind. Eng. Chem. Process Des. Develop., **8** (1969) 450.
14. Schepple, S. E., Greenwood, G. J., Benson, P. A.: Anal. Chem., **49** (1977) 1847.
15. Aczel, T., Lumpkin, H. E.: Preprints, Div. Petrol. Chem. Am. Chem. Soc., **22**(3) (1977) 911.
16. Schultz, J. L., Friedel, R. A., Sharkey, A. G.: Mass Spectrometric Analysis of Colal Tar Distillates and Residues, Bureau of Mines Report on Investigation No. 7000, U. S. Dept. of Interior, 1967.
17. Gulf Reasearch & Development Company, Gulf Process Brochure – Hydrocarbon Processes and Catalysts, Pittsburgh, PA, 1975.
18. J. P. Wauquier, Petroleum Refining (Crude oil, Petroleum Products, Process Flowsheets), Editions Technip, Paris, 1995.
19. Schuman, S. C., Shalit, H.: Catal. Rev., **4**(2) (1970) 245.
20. Shuit, G. C. A., Gates, B. C.: AIChE J., **19**(3) (1973) 417.

21. Metcalfe, T. B.: Hydrogen Sulfided Inhibition of Hydrodesulfurization, Presented at AIChE 64th National Meeting, New Orleans, Louisiana, 1969.

22. M. Absi Halabi, J. Beshara, H. Qabazard, A. Stanislaus, Catalysts in Petroleum Refining and Petrochemical Industries, Elseiver, Amsterdam, 1996

23. Paraskos, J. A., Frayer, J. A., Shah, Y. T.: Ind. Eng. Chem., Process Des. Dev., **14** (1975) 315

24. Magee, J., Dolbear, G.: Petroleum Catalysis in Nontechnical Language, TennWell Publishing Company, Tulsa, 1998.

25. Hobson, G. D.: Modern Petroleum Technology, John Wiley & Sons, London, 1984.

26. H. F. Rase, *Handbook of Commercial Catalysts, Heterogeneous Catalysts*, CRC Press, 2000.

Autori / Authors:

dr. sc. prof. Katica Sertić Bionda, dipl.ing., Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu

Tomislav Šarić, dipl.ing., INA SSRII Zagreb

Marko Mužic, dipl.ing., Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu