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## MODELIRANJE PROCESA IZOMERIZACIJE U SVRHU POBOLJŠANJA KAKVOĆE MOTORNIH BENZINA

### Sažetak

*U radu je postavljen matematički model odabranog modela izomerizacije. Pri postavljanju modela proces je istražen sa stajališta reakcijskog mehanizma, kinetike reakcija izomerizacije, te parametara kemijske ravnoteže. Simulacijski model reaktora izveden je prema postavljenim materijalnim bilancama, a modelom su opisani i procesi izmjene topline, te procesi izmjene tvari postupcima separacije.*

*Postavljeni simulacijski model omogućio je istraživanje i proučavanje optimalnih radnih uvjeta procesa simuliranjem, te je predloženo unapređenje procesa sa stajališta povećanja prinosa visokooktanskog produkta procesa izomerizacije, kao i povećanja oktanskog broja proizvoda.*

*Rezultati dobiveni simuliranjem procesa unaprijeđenog dodatkom kolone za deizopentanizaciju pokazali su povećanje iscrpka izomerizata za čak 42% u usporedbi s procesom bez unapređenja, dok je izvedba procesa s molekulskim sitima rezultirala značajnim povećanjem istraživačkog oktanskog broja proizvoda od 9 jedinica. Rezultati simuliranja procesa bez unapređenja i procesa s kolonom deizopentanizera pokazali su vrlo dobro slaganje s eksperimentalnim podacima industrijskog procesa.*

### 1.0. Uvod

Proces izomerizacije zauzima značajno mjesto u proizvodnji motornih benzina zbog svoje uloge u poboljšanju primjenskih svojstava frakcije lakog benzina. Procesom dolazi do konverzije n-spojeva (butan, pentan, heksan) u izospojeve, čime se povećava oktanski broj lakog benzina.<sup>1</sup>

Prvi rezultati istraživanja izomerizacije kao katalitičkog procesa dobiveni su već 30-ih godina prošloga stoljeća. Potreba za visokooktanskim benzinom za zrakoplove tijekom II. svjetskog rata uvjetovala je daljnji napredak procesa izomerizacije. Kraći lanci olefina proizvedeni fluid katalitičkim krekingom bili su pogodna sirovina za alkilaciju izobutanom ( $i\text{-C}_4$ ) i dobivanje produkta visokog oktanskog broja. Izvori i proizvodnja izobutana nisu bili dovoljni za zadovoljavanje novih potreba, pa je bilo potrebno pronaći novo rješenje. Izomerizacija normalnog lanca parafina u izobutan zadovoljila je navedene potrebe.<sup>2</sup>

Prva industrijska postrojenja počela su radom 1941. u SAD-u, a temeljila su se na kemiji Friedel-Craftsovih katalizatora. Ta postrojenja zadovoljila su trenutačne potrebe, no svojstva katalizatora utjecala su na značajnu pojavu korozije, veliku potrošnju katalizatora, te značajne proizvodne troškove.<sup>2</sup>

Otkriće bifunkcionalnih katalizatora<sup>2</sup>, prije svega za potrebe procesa katalitičkog reforminga, dalo je logične smjernice za razvoj procesa izomerizacije.

Težnja za sve boljom kvalitetom i većim količinama motornih benzina bila je pokretač daljnjeg razvoja ovog procesa. Nakon 80-ih godina postignuta su najveća poboljšanja, a posebno što se tiče katalizatora. Napredak je ubrzala činjenica da su se dotad najviše primjenjivani poboljšivači oktanskog broja na osnovi spojeva olova: tetre-etil-olovo (TEO;  $\text{Pb}(\text{C}_2\text{H}_5)_4$ ) i tetra-metil-olovo (TMO;  $\text{Pb}(\text{CH}_3)_4$ ), počeli povlačiti iz uporabe, zbog svojih štetnih utjecaja na okoliš. Ta činjenica pridonijela je važnosti razvoja procesa izomerizacije.

Današnji su trendovi razvoja procesa izomerizacije usredotočeni na unapređenje procesa u svrhu poboljšanja kakvoće motornih benzina. Ovim se radom nastojalo naglasiti važnost i primjenu unapređenja procesa modeliranjem.

## 2.0. Eksperimentalni dio

### 2.1. Sirovina i katalizator

Sirovina: Laki benzin dobiven atmosferskom destilacijom. Kemijski sastav prikazan je tablicom 1.

Katalizator: Platina na nosaču  $\text{Al}_2\text{O}_3$ , uz kloride kao promotore kisele funkcije ( $\text{HCl}$ ,  $\text{CCl}_4$ ), uz prisutnost vodika.

### 2.2. Opis procesa

Spojevi poput vode, sumporovih spojeva ili nezasićenih ugljikovodika smanjuju aktivnost katalizatora kao i njegovu selektivnost. Zbog toga se prije procesa izomerizacije sirovina obrađuje, hidrodesulfurizacijom i hidrogenacijom. Tako pripremljena sirovina ulazi u proces izomerizacije shematski prikazan slikom 1.

Tok šarže nakon obrade vodikom dijeli se u dva dijela. Prvi tok, manji, odvodi se u apsorber, V-401, u kojem se sakuplja  $\text{HCl}$  iz plinske faze. Apsorpcijska kapljevina,

zajedno s HCl-om s dna posude V-401, odvodi se u tok šarže izomerizacije. S vrha apsorbera se plinovita faza odvodi u sustav plina za loženje.

Drugi, veći tok šarže izomerizacije, miješa se s recirkulirajućim plinom izomerizacije i provodi se kroz izmjenjivače E-401ABC i E-402, te uvodi u reaktor R-401. Izlazni tok reaktora R-401, nakon hlađenja u E-401ABC i u EA-403 provodi se u visokotlačni separator V-403. Plinovita faza s vrha separatora odvodi se u usisnu posudu kompresora V-404, a zatim na usis kompresora K-401A/B.

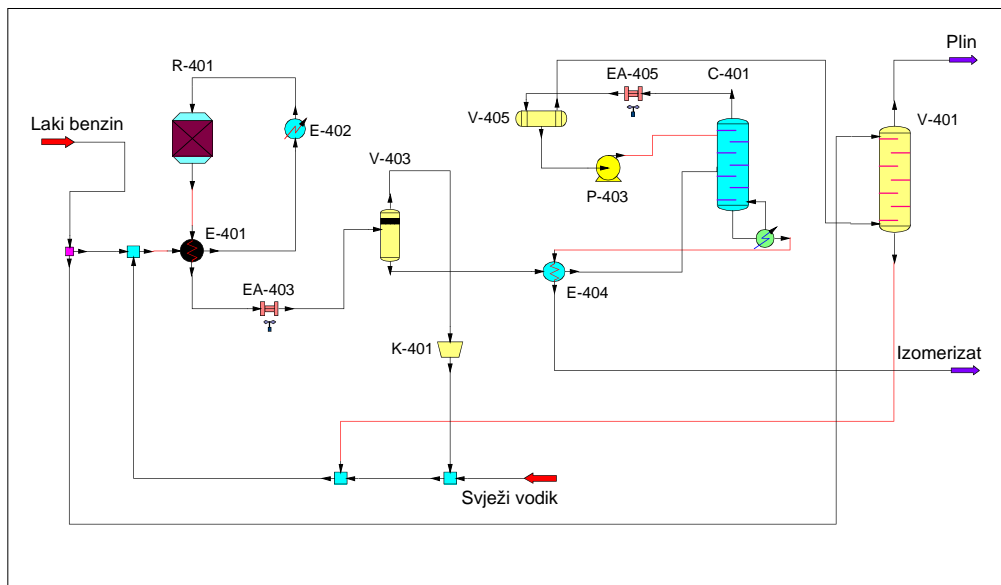
Tablica 1: Sastav sirovine

| Komponenta       | Sastav sirovine |              |
|------------------|-----------------|--------------|
|                  | kmol/h          | mol. udio    |
| Vodik            | 6.97            | 0.019        |
| Klorovodik       | 0.00            | 0.000        |
| Sumporovodik     | 0.00            | 0.000        |
| Metan            | 1.47            | 0.004        |
| Etan             | 0.02            | 0.000        |
| Propan           | 0.02            | 0.000        |
| i-butan          | 0.19            | 0.001        |
| n-butan          | 1.98            | 0.005        |
| i-pentan         | 117.68          | 0.320        |
| n- pentan        | 117.53          | 0.320        |
| 2,2-dimetilbutan | 0.36            | 0.001        |
| 2,3-dimetilbutan | 4.38            | 0.012        |
| 2-metilpentan    | 34.05           | 0.093        |
| 3-metilpentan    | 25.75           | 0.070        |
| n-heksan         | 47.61           | 0.129        |
| Benzen           | 0.00            | 0.000        |
| Metilciklopentan | 7.52            | 0.020        |
| Cikloheksan      | 2.17            | 0.006        |
| <b>Ukupno:</b>   | <b>367.72</b>   | <b>1.000</b> |

Kapljevita faza s dna posude V-403 odvodi se u izmjenjivače E-404A/B, gdje se grije izomerizatom s dna kolone C-401, a zatim u striper klorovodika, C-401. Pare s vrha kolone C-401, koje sadrže HCl, vodik i lake ugljikovodike, kondenziraju u kondenzatoru EA-405. Ukapljeni dio se skuplja u posudi V-405 i vraća pomoću crpke P-402A/B kao pretok u kolonu C-401.

S vrha posude V-405 pare koje sadrže HCl odvođe se u apsorber V-401. Proizvod dna stripera C-401, izomerizat, nakon hlađenja u E-404A/B i zračnom hladnjaku EA-407, uvodi se u posudu za pranje lužinom.

Slika 1: Shema procesa izomerizacije



### 2.3. Izgradnja i prilagodba simulacijskog modela

Za svladavanje svih utjecajnih djelovanja, na osnovi sustavnog pristupa<sup>3</sup> postavlja se simulacijski model procesa, matematički model izrađen u programskom sustavu za simuliranje procesa ChemCad.<sup>4</sup> Matematički model reaktora, u programskom sustavu ChemCad, predstavljen je u općem obliku. To podrazumijeva definiranje ravnoteže, kinetike i stehiometrije kemijskih reakcija.<sup>5,6</sup>

### 3.0. Rezultati i rasprava

U radu su uspoređeni rezultati simulacijskog modela s eksperimentalnim podacima pri istim radnim uvjetima u industrijskom procesu. Postavljanjem simulacijskog modela stvorena je osnova za predodžbu unapređenja, kao i provedbu dodatnih istraživanja procesa.

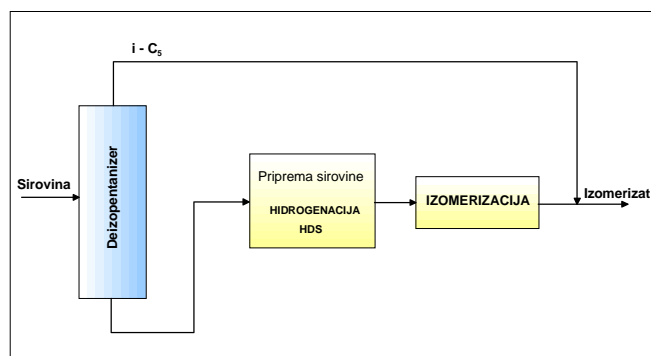
U eksperimentalnom dijelu rada simulacijski model reaktora postavljen je prema kinetičkim i parametrima kemijske ravnoteže reakcija. Pri izradi simulacijskog modela primjenjivane su izračunate veličine dobivene prilagodbom iz eksperimentalnih podataka i jednadžbi za ukupnu bilancu reaktora, kao i za bilance pojedinačnih komponenata. Model reaktora izveden je pomoću programskog sustava za rješavanje sustava linearnih i nelinearnih jednadžbi Lingo.<sup>7</sup>

### 3.1. Pristup unapređenju procesa

S obzirom na važnost i namjenu procesa izomerizacije, temeljni cilj rada bio je utvrditi mogućnosti poboljšanja kakvoće, kao i iscrpka izomerizata. U tom smislu provedeno je unapređenje osnovne izvedbe procesa na dva načina koja su opisana u daljnjem tekstu.

#### 1. Pretfrakcionacija sirovine prije procesa izomerizacije

Slika 2: Unapređenje s pretfrakcionacijom sirovine u deizopentanizeru



U sirovini koja ulazi u proces izomerizacije postoji znatna količina izopentana. Ukoliko bi se ta količina smanjila, moguće je povećati kapacitet postrojenja i dobiti veći iscrpak. Veća količina iscrpka dobiva se miješanjem proizvoda vrha deizopentanizera s produktom procesa izomerizacije, izomerizatom. Unapređenje ovim procesom temelji se na promjeni sastava sirovine na ulazu u proces, sastava prikazanog tablicom 2, a sheme procesa prikazane slikom 2.

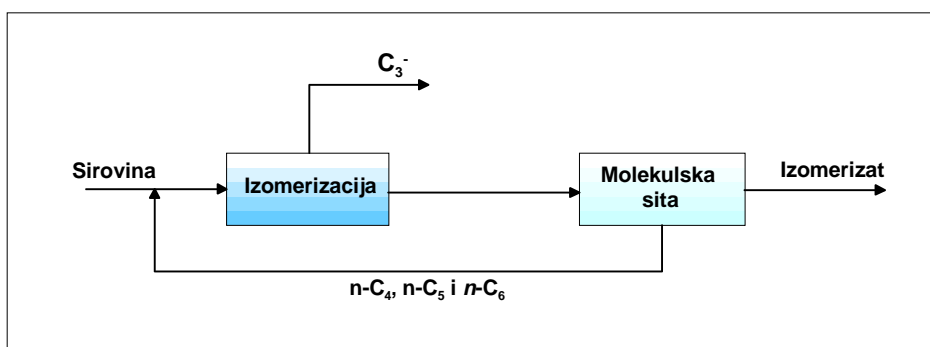
#### 2. Povrat normalnih lanaca ugljikovodika u proces separacijom kroz molekulska sita

Povratom n-ugljikovodika i njihovom daljnjom konverzijom u izospojeve omogućava se povišenje oktanskog broja produkta. Shema procesa prikazana je slikom 3.

Tablica 2: Sastav sirovine prethodno obrađene u deizopentanizeru

| Komponenta       | Sastav sirovine |              |
|------------------|-----------------|--------------|
|                  | kmol/h          | mol.udio     |
| Vodik            | 6.30            | 0.017        |
| Klorovodik       | 0.00            | 0.000        |
| Sumporovodik     | 0.00            | 0.000        |
| Metan            | 5.68            | 0.016        |
| Etan             | 0.02            | 0.000        |
| Propan           | 0.00            | 0.000        |
| i-butan          | 0.00            | 0.000        |
| n-butan          | 0.00            | 0.000        |
| i-pentan         | 40.55           | 0.111        |
| n- pentan        | 130.75          | 0.358        |
| 2,2-dimetilbutan | 0.52            | 0.001        |
| 2,3-dimetilbutan | 6.59            | 0.018        |
| 2-metilpentan    | 51.27           | 0.140        |
| 3-metilpentan    | 38.56           | 0.106        |
| n-heksan         | 70.00           | 0.192        |
| Benzen           | 0.01            | 0.000        |
| Metilciklopentan | 11.28           | 0.031        |
| Cikloheksan      | 3.65            | 0.010        |
| <b>Ukupno:</b>   | <b>365.17</b>   | <b>1.000</b> |

Slika 3: Shema procesa unaprijeđenog molekularnim sitima



Tablica 3: Sastav izomerizata za tri različita simulacijska modela procesa izomerizacije

| Komponenta       | Proces bez unapređenja |          | Proces s molekulskim sitima |          | Proces s deizopentanizerom (DIP) |          |
|------------------|------------------------|----------|-----------------------------|----------|----------------------------------|----------|
|                  | kmol/h                 | mol.udio | kmol/h                      | mol.udio | kmol/h                           | mol.udio |
| Vodik            | 0.01                   | 0.000    | 0.00                        | 0.000    | 0.05                             | 0.000    |
| Klorovodik       | 0.05                   | 0.000    | 0.00                        | 0.000    | 0.00                             | 0.000    |
| Sumporovodik     | 0.00                   | 0.000    | 0.00                        | 0.000    | 0.00                             | 0.000    |
| Metan            | 0.33                   | 0.001    | 0.00                        | 0.000    | 2.73                             | 0.008    |
| Etan             | 0.22                   | 0.001    | 0.02                        | 0.000    | 0.31                             | 0.001    |
| Propan           | 0.86                   | 0.002    | 1.18                        | 0.003    | 1.23                             | 0.003    |
| i-butan          | 1.92                   | 0.005    | 3.21                        | 0.009    | 1.13                             | 0.000    |
| n-butan          | 0.69                   | 0.002    | 0.00                        | 0.000    | 6.30                             | 0.001    |
| i-pentan         | 152.19                 | 0.424    | 230.97                      | 0.649    | 222.96                           | 0.324    |
| n-pentan         | 81.66                  | 0.227    | 0.00                        | 0.000    | 105.36                           | 0.155    |
| 2,2-dimetilbutan | 31.13                  | 0.087    | 42.78                       | 0.120    | 45.917                           | 0.129    |
| 2,3-dimetilbutan | 12.75                  | 0.036    | 13.70                       | 0.038    | 19.15                            | 0.054    |
| 2-metilpentan    | 36.19                  | 0.101    | 37.00                       | 0.104    | 54.43                            | 0.153    |
| 3-metilpentan    | 20.03                  | 0.056    | 20.07                       | 0.056    | 29.87                            | 0.084    |
| n-heksan         | 13.81                  | 0.038    | 0.00                        | 0.000    | 20.19                            | 0.057    |
| Benzen           | 0.00                   | 0.000    | 0.00                        | 0.000    | 0.00                             | 0.000    |
| Metilciklopentan | 3.98                   | 0.011    | 3.99                        | 0.011    | 5.93                             | 0.017    |
| Cikloheksan      | 3.23                   | 0.009    | 3.22                        | 0.009    | 5.25                             | 0.015    |
| Ukupno:          | 359.03                 | 1.000    | 356.13                      | 1.000    | 520.81                           | 1.000    |

### 3.2. Rezultat unapređenja

Tablicom 3 prikazani su sastavi izomerizata dobiveni simuliranjem tri različita procesa izomerizacije. Rezultati procesa s molekulskim sitima pokazuju, u odnosu na proces bez unapređenja, očekivano povećanje molarnog udjela izospojeva (izopentan, 2,2-dimetilbutan, 2,3-dimetilbutan i 2 metilpentan), bez prisutnosti n-pentana i n-heksana u izomerizatu.

Rezultati dobiveni simulacijskim modelom prikazani su u usporedbi s eksperimentalnim podacima za proces bez unapređenja, kao i za poboljšan proces uvođenjem kolone za deizopentanizaciju u tablici 4. Vidljivo je da se rezultati dobiveni simuliranjem dobro slažu s eksperimentalnim podacima industrijskog procesa.

Tablica 4: Sastav produkata procesa izomerizacije: usporedba rezultata simulacijskog modela procesa izomerizacije s eksperimentalnim podacima

| Komponenta       | Procez bez unapređenja    |                                 | Proces s deizopentanizerom |                                   |
|------------------|---------------------------|---------------------------------|----------------------------|-----------------------------------|
|                  | Eksp. podaci<br>mol. udio | Simulacijski<br>model, mol.udio | Eksp. podaci<br>mol. udio  | Simulacijski<br>model, mol. udio. |
| Vodik            | 0.000                     | 0.000                           | 0.000                      | 0.000                             |
| Klorovodik       | 0.000                     | 0.000                           | 0.000                      | 0.000                             |
| Sumporovodik     | 0.000                     | 0.000                           | 0.000                      | 0.000                             |
| Metan            | 0.000                     | 0.001                           | 0.000                      | 0.008                             |
| Etan             | 0.001                     | 0.001                           | 0.001                      | 0.001                             |
| Propan           | 0.002                     | 0.002                           | 0.002                      | 0.003                             |
| i-butan          | 0.006                     | 0.005                           | 0.006                      | 0.000                             |
| n-butan          | 0.005                     | 0.002                           | 0.000                      | 0.001                             |
| i-pentan         | 0.427                     | 0.424                           | 0.316                      | 0.324                             |
| n- pentan        | 0.221                     | 0.227                           | 0.164                      | 0.155                             |
| 2,2-dimetilbutan | 0.087                     | 0.087                           | 0.139                      | 0.129                             |
| 2,3-dimetilbutan | 0.035                     | 0.036                           | 0.054                      | 0.054                             |
| 2-metilpentan    | 0.101                     | 0.101                           | 0.153                      | 0.153                             |
| 3-metilpentan    | 0.055                     | 0.056                           | 0.084                      | 0.084                             |
| n-heksan         | 0.038                     | 0.038                           | 0.057                      | 0.057                             |
| Benzen           | 0.000                     | 0.000                           | 0.000                      | 0.000                             |
| Metilciklopentan | 0.011                     | 0.011                           | 0.017                      | 0.017                             |
| Cikloheksan      | 0.009                     | 0.009                           | 0.013                      | 0.015                             |
| Ukupno:          | 1.000                     | 1.000                           | 1.000                      | 1.000                             |

Kako je temeljni cilj procesa izomerizacije povećanje oktanskog broja, i saznanja ove provedene analize poslužila za dobivanje rezultata o toj važnoj značajki.

Tablica 5 pokazuje oktanske brojeve sirovine i izomerizata. Navedene promjene sastava daju značajno povećanje vrijednosti istraživačkog oktanskog broja za čak 9 jedinica, ili oko 12%. S druge pak strane, proces izomerizacije sa smanjenim udjelom izopentana u sirovini, daje neznatno viši istraživački oktanski broj (tablica 5), što je u skladu s odgovarajućim razlikama u sastavu, posebno na molarnom udjelu izospojeva u produktima.



Tablica 5: Oktanski brojevi izomerizata

| Procesni tok                 | Istraživački oktanski broj smjese (IOB) | Motorni oktanski broj smjese (MOB) |
|------------------------------|---|------------------------------------|
| Sirovina                     | 68.6                                    | 68.2                               |
| Izomerizat                   |   |                                    |
| Proces bez unapređenja       | 79.4                                    | 77.8                               |
| Proces s molekularnim sitima | 88.9                                    | 87.7                               |
| Proces s deizopentanizerom   | 79.9                                    | 79.6                               |

Za potpunu analizu procesa potrebno je znati podatak o dobivenoj količini izomerizata. Protoci izomerizata u m<sup>3</sup>/h pri standardnim uvjetima tlaka i temperature prikazani su tablicom 6. Vidljivo je da je volumni protok izomerizata procesa s molekulskim sitima gotovo jednak osnovnom procesu. Međutim, izvedbom procesa s molekulskim sitima postiže se značajno poboljšanje iscrpka izomerizata, te je volumni protok od 62.3 m<sup>3</sup>/h, čak za 45% veći u odnosu na proces bez unapređenja.

Tablica 6: Volumni protoci izomerizata

| Izomerizat                   | Volumni protok, Std m <sup>3</sup> /h |
|------------------------------|---------------------------------------|
| Proces bez unapređenja       | 43.0                                  |
| Proces s molekularnim sitima | 42.8                                  |
| Proces s deizopentanizerom   | 62.3                                  |

U slučaju odabira procesa s molekulskim sitima, osim nadogradnje molekulskih sita, treba voditi računa i o promjeni radnih uvjeta do kojih dolazi ugradnjom ove procesne jedinice. Naime, povratnim tokom iz molekulskih sita, druge procesne jedinice se dodatno opterećuju većim volumnim protokom, te dolazi do promjene prostorne brzine i u reaktoru. Tako je porast volumnog protoka primjerice za reaktor čak 42%. To je vrlo velika promjena volumnog protoka, koja zahtijeva ugrađivanje novog reaktora, što je potrebno dodatno istražiti. Utjecaj na ostale procesne jedinice također je potrebno pažljivo proučiti.

S druge pak strane, proces koji koristi sirovinu sa smanjenim sadržajem izopentana zahtijeva samo dodatnu kolonu s njezinom sporednom procesnom opremom. Time se u istom postrojenju omogućuje prerada više niskooktanske sirovine. Miješanjem proizvoda vrha deizopentanizera s produktom procesa, izomerizatom, dobiva se veći iscrpak.

Dakle, izvedba s deizopentanizerom čini se jednostavnijom i prihvatljivijom, ali kako je za rafinerije nafte glavni cilj povišenje oktanskog broja, izvedbu s molekulskim sitima ipak je potrebno istražiti.

## 5.0. Zaključci

Na osnovi eksperimentalnih podataka s industrijskog procesa postavljen je simulacijski model reaktora i cjelovitog procesa izomerizacije, primjenom programskog sustava za rješavanje sustava linearnih i nelinearnih jednadžbi Lingo, te programskog sustava za simuliranje procesa ChemCad. Provedene su određene usporedbe različitih procesa s ciljem poboljšanja oktanskog broja i iscrpka izomerizata, sve u svrhu poboljšanja kakvoće motornih benzina.

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

- Usporedbom eksperimentalnih podataka i podataka simulacijskih modela vidljive se promjene sastava izomerizata u odnosu na ulaznu sirovinu, koja se očituje povećanjem molarnih udjela izospojeva (izopentan, 2,2-dimetilbutan, 2,3-dimetilbutan, 2-metilpentan, 3-metilpentan), kao i smanjenjem udjela n-pentana i n-heksana.
- Rezultati simuliranja poboljšanog procesa prefrakcionacijom sirovine u koloni za deizopentanizaciju pokazali su povećanje volumnog protoka izomerizata za 45% u odnosu na osnovni proces. Pritom je došlo do vrlo malog povećanja vrijednosti IOB.
- Poboljšanje procesa dodatkom molekulskih sita, čime je omogućen povrat ravnolančanih ugljikovodika u sirovinu, rezultiralo je povećanjem IOB izomerizata za 9 jedinica, pri gotovo istovjetnom protoku izomerizata, u usporedbi s procesom bez poboljšanja.
- Rezultati simuliranja provedenih izvedbi procesa izomerizacije pokazali su vrlo dobra slaganja s eksperimentalnim podacima industrijskog procesa.
- U radu nisu razmatrani ekonomski aspekti navedenih poboljšanja, ali se može pretpostaviti da je izvedba s kolonom za deizopentanizaciju prihvatljivija, ukoliko postizanje vrlo visokih vrijednosti IOB ne predstavlja primaran rafinerijski problem. S druge pak strane, izvedba procesa s molekulskim sitima zahtijeva dodatnu analizu procesa i provedbu dimenzioniranja procesnih jedinica i uređaja.

# MODELLING OF THE ISOMERIZATION PROCESS FOR THE PURPOSE OF ADVANCING MOTOR GASOLINE QUALITY

## *Abstract*

*The paper defines a mathematical model of the chosen isomerization model. While setting the model, the process was explored from the viewpoint of reaction mechanism, isomerization reactions kinetics, and chemical balance parameters. The reactor simulation model has been elaborated according to the set material balances, while the model describes also the heat exchange processes, as well as those of substance exchange using separation procedures.*

*The set simulation model has enabled research and study of optimal operating process conditions using simulation, and process advancement has been suggested from the viewpoint of increasing the yield of the high octane isomerization process product, as well as the yield of the product octane number.*

*The results obtained through the simulation of the process advanced by the addition of the deisopentanizer column have shown an increased isomerate yield by as much as 42% compared with the process without advancement, while the process implementation with molecular sieves has resulted in a considerable increase of the product research octane number of 9 units. The results of process simulation without advancement and those of the process with deisopentanizer column have shown very good match with the experimental data of the industrial process.*

## 1.0. Introduction

The isomerization process has an important position in the production of motor gasoline due to its role in the improvement of the light gasoline fraction applicative properties. The process causes a conversion of n-paraffins (butane, pentane, hexane) into iso-paraffins, thus increasing the octane number of the light gasoline.<sup>1</sup>

The initial results of exploring isomerization as a catalytic process were obtained back in the 30's of the past century. The need for a high octane gasoline for airplanes in the course of WWII conditioned a further advancement of the process isomerization process. Shorter olefin chains produced through fluid catalytic cracking were a suitable feed for alkylation using isobutane (i-C<sub>4</sub>) and obtaining products with high octane number. The sources and production of isobutane were

not sufficient for meeting new needs, which is why a new solution had to be found. The isomerization of normal paraffin chain into isobutane has met the said needs.<sup>2</sup>

The first industrial plants began operating in 1941 in the USA, based on the chemistry of Friedel–Crafts catalysts. These plants managed to meet the needs of the moment, but the catalyst properties caused a major corrosion appearance, high catalyst consumption, and considerable production costs.<sup>2</sup>

The discovery of bifunctional catalysts<sup>2</sup>, primarily for the needs of the catalytic reforming process, has provided logical guidelines for the isomerization process development.

The desire for improved quality and higher volumes of motor gasoline was the motivation for the process' further development. The greatest improvements were achieved after the 80's, especially when it comes to catalysts. The progress was speeded up by the fact that the octane number improvers based on lead compounds which were used the most until then: tetra-ethyl-lead (TEO;  $\text{Pb}(\text{C}_2\text{H}_5)_4$ ) and tetra-methyl-lead (TMO;  $\text{Pb}(\text{CH}_3)_4$ ), started to be phased out, due to their harmful environmental impact. This fact has contributed to the importance of the isomerization process development.

Today's trends of the isomerization process development are oriented towards process advancement for the purpose of improving the quality of motor gasoline. It is the intention of the present paper to stress the importance and the application of process advancement using modelling.

## 2.0. The Experimental Part

### 2.1. The Feed and the Catalyst

Feed: Light gasoline obtained through atmospheric distillation. The chemical composition is shown in Table 1.

Catalyst: Platinum on  $\text{Al}_2\text{O}_3$  bearer, with chlorides as acid function promoters ( $\text{HCl}$ ,  $\text{CCl}_4$ ), with the presence of hydrogen.

### 2.2. The Process Description

Compounds like water, sulphur compounds or unsaturated hydrocarbons reduce the catalyst's activity, as well as its selectivity. That is why before the isomerization process the feed is being treated, through hydrodesulphurising i hydrogenation. Thus prepared feed enters the isomerization process outlined in Figure 1.

The charge flow following the hydrogen treatment proceeds in two parts. The first flow, which is smaller, is conducted into the absorber, V-401, where  $\text{HCl}$  is being collected from the gaseous phase. The absorption fluid, together with  $\text{HCl}$  from the bottom of the vessel V-401, is conducted into the isomerization charge flow. From the top of the absorber, the gaseous phase is conducted into the fuel gas system.

The other, larger isomerization charge flow is mixed with the isomerization recycle gas, conducted through exchangers E-401ABC and E-402, and introduced into the

R-401 reactor. The output flow of the reactor R-401 is, after cooling in E-401ABC and in EA-403, conducted to the high pressure separator V-403. The gaseous phase from the separator top is conducted into the suction vessel of compressor V-404, and then to the suction point of compressor K-401A/B.

Table 1: Feed composition

| Component          | Feed composition |               |
|--------------------|------------------|---------------|
|                    | kmol/h           | mole fraction |
| Hydrogen           | 6.97             | 0.019         |
| Hydrogen chloride  | 0.00             | 0.000         |
| Hydrogen sulphide  | 0.00             | 0.000         |
| Methane            | 1.47             | 0.004         |
| Ethane             | 0.02             | 0.000         |
| Propane            | 0.02             | 0.000         |
| i-butane           | 0.19             | 0.001         |
| n-butane           | 1.98             | 0.005         |
| i-pentane          | 117.68           | 0.320         |
| n- pentane         | 117.53           | 0.320         |
| 2,2-dimethylbutane | 0.36             | 0.001         |
| 2,3-dimethylbutane | 4.38             | 0.012         |
| 2-methylpentane    | 34.05            | 0.093         |
| 3-methylpentane    | 25.75            | 0.070         |
| n-hexane           | 47.61            | 0.129         |
| Benzene            | 0.00             | 0.000         |
| Methylcyclopentane | 7.52             | 0.020         |
| Cyclohexane        | 2.17             | 0.006         |
| Total:             | 367.72           | 1.000         |

The liquid phase from the bottom of the vessel V-403 is conducted to the exchangers E-404A/B, where it is heated by the isomerizate from the bottom of the column C-401, and further on to the hydrogen chloride stripper, C-401. The vapour from the top of the column C-401, containing HCl, hydrogen and light hydrocarbons, are being condensated in the condenser EA-405. The liquid part is collected in the vessel V-405 and returned using pump P-402A/B as reflux into the column C-401.

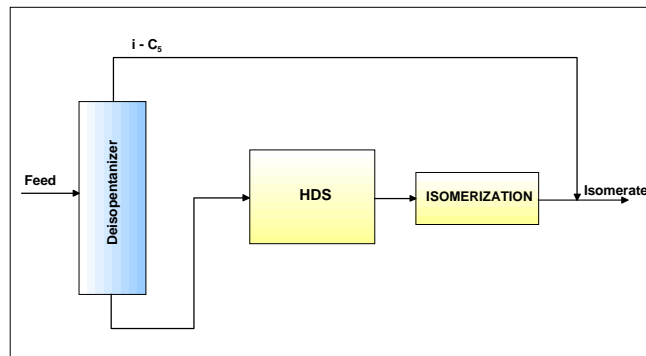
From the top of the V-405 vessel, the vapours containing HCl are conducted into the absorber V-401. The product from the bottom of the stripper C-401, the isomerizate, after cooling in E-404A/B, and the air refrigerator EA-407, is introduced into the washing vessel using alkali.



### 3.1. Approach to the Process Advancement

Given the importance and the purpose of the isomerization process, the basic goal of the paper was to identify the possibility of improving the quality, as well as the yield of isomerate. To this end, the advancement of the basic process implementation was performed in two ways described in further text.

Figure 2: Advancement with feed prefractionation in the deisopentimizer



#### 1. Prefractionation of Feed Before the Isomerization Process

The feed entering the isomerization process contains a considerable volume of isopentane. Should this volume be reduced, it would be possible to increase the plant's capacity and obtain higher yield. Higher yield volume is obtained by mixing the product from the top of the deisopentimizer with the isomerization process product, the isomerate.

The advancement using this particular process is based on changing feed composition at the entrance into the process; composition shown in Table 2, and process outline shown in Figure 2.

Figure 3: Outline of the process advanced by molecular sieves

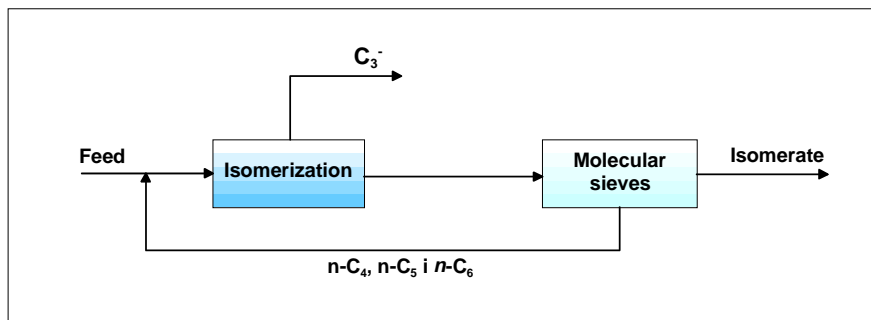


Table 2: Composition of feed previously treated in deisopentanizer

| Component          | Feed composition |               |
|--------------------|------------------|---------------|
|                    | kmol/h           | mole fraction |
| Hydrogen           | 6.30             | 0.017         |
| Hydrogen chloride  | 0.00             | 0.000         |
| Hydrogen sulphide  | 0.00             | 0.000         |
| Methane            | 5.68             | 0.016         |
| Ethane             | 0.02             | 0.000         |
| Propane            | 0.00             | 0.000         |
| i-butane           | 0.00             | 0.000         |
| n-butane           | 0.00             | 0.000         |
| i-pentane          | 40.55            | 0.111         |
| n-pentane          | 130.75           | 0.358         |
| 2,2-dimethylbutane | 0.52             | 0.001         |
| 2,3-dimethylbutane | 6.59             | 0.018         |
| 2-methylpentane    | 51.27            | 0.140         |
| 3-methylpentane    | 38.56            | 0.106         |
| n-hexane           | 70.00            | 0.192         |
| Benzene            | 0.01             | 0.000         |
| Methylcyclopentane | 11.28            | 0.031         |
| Cyclohexane        | 3.65             | 0.010         |
| Total:             | 365.17           | 1.000         |

## 2. Return of n-paraffins into the process using separation by molecular sieves

The return of n-paraffins and their further conversion into iso-paraffins enables increase of the product's octane number. The process outline is shown in Figure 3.

### 3.2. The Advancement Result

Table 3 shows the compositions of the isomerate obtained by simulating three different isomerization processes. Results of the process with molecular sieves show – with regard to the process without advancement, the expected increase of the iso-compounds (isopentane, 2,2-dimethylbutane, 2,3-dimethylbutane and 2 methylpentane) mole fractions, without the presence of n-pentane or n-hexane in the isomerate.

The results obtained by the simulation model are shown in comparison with the experimental data for the process without advancement, as well as for the process improved by introducing the column for deisopentanization in Table 4. It may be observed that the results obtained by simulation match well with the experimental data of the industrial process.



Table 3: Composition of isomerate for three different simulation models of the isomerization process

| Component          | Process without advancement |               | Process with molecular sieves |               | Process with deisopentanizer (DIP) |               |
|--------------------|-----------------------------|---------------|-------------------------------|---------------|------------------------------------|---------------|
|                    | kmol/h                      | mole fraction | kmol/h                        | mole fraction | kmol/h                             | mole fraction |
| Hydrogen           | 0.01                        | 0.000         | 0.00                          | 0.000         | 0.05                               | 0.000         |
| Hyd. chloride      | 0.05                        | 0.000         | 0.00                          | 0.000         | 0.00                               | 0.000         |
| Hyd. sulphide      | 0.00                        | 0.000         | 0.00                          | 0.000         | 0.00                               | 0.000         |
| Methane            | 0.33                        | 0.001         | 0.00                          | 0.000         | 2.73                               | 0.008         |
| Ethane             | 0.22                        | 0.001         | 0.02                          | 0.000         | 0.31                               | 0.001         |
| Propane            | 0.86                        | 0.002         | 1.18                          | 0.003         | 1.23                               | 0.003         |
| i-butane           | 1.92                        | 0.005         | 3.21                          | 0.009         | 1.13                               | 0.000         |
| n-butane           | 0.69                        | 0.002         | 0.00                          | 0.000         | 6.30                               | 0.001         |
| i-pentane          | 152.19                      | 0.424         | 230.97                        | 0.649         | 222.96                             | 0.324         |
| n- pentane         | 81.66                       | 0.227         | 0.00                          | 0.000         | 105.36                             | 0.155         |
| 2,2-dimethylbutane | 31.13                       | 0.087         | 42.78                         | 0.120         | 45.917                             | 0.129         |
| 2,3-dimethylbutane | 12.75                       | 0.036         | 13.70                         | 0.038         | 19.15                              | 0.054         |
| 2-methylpentane    | 36.19                       | 0.101         | 37.00                         | 0.104         | 54.43                              | 0.153         |
| 3-methylpentane    | 20.03                       | 0.056         | 20.07                         | 0.056         | 29.87                              | 0.084         |
| n-hexane           | 13.81                       | 0.038         | 0.00                          | 0.000         | 20.19                              | 0.057         |
| Benzene            | 0.00                        | 0.000         | 0.00                          | 0.000         | 0.00                               | 0.000         |
| Metylcyclopentane  | 3.98                        | 0.011         | 3.99                          | 0.011         | 5.93                               | 0.017         |
| Cyclohexane        | 3.23                        | 0.009         | 3.22                          | 0.009         | 5.25                               | 0.015         |
| Total:             | 359.03                      | 1.000         | 356.13                        | 1.000         | 520.81                             | 1.000         |

Since the basic goal of the isomerization process is the octane number increase, the results of the analysis performed have contributed to obtaining information on this important property.

Table 5 indicates octane numbers of the feed and the isomerate. The above changes in composition provide a considerable increase of the research octane number by as much as 9 units or around 12%. On the other hand, the isomerization process with a reduced isopentane share in the feed provides a slightly higher RON (Table 5), which is consistent with the corresponding differences in composition, especially the mole fraction of iso-paraffins in products.

For a complete analysis of the process one must know the obtained isomerate volume. Isomerate flows in m<sup>3</sup>/h at standard pressure and temperature conditions are shown in Table 6. One may observe that the isomerate flowrate of the process with molecular sieves is nearly the same as the basic process. However, the process with molecular sieves obtains a considerable improvement of the isomerate

yield, and the volumetric flow of 62.3 m<sup>3</sup>/h, is as much as 45% higher with regard to the process without advancement.

Table 4: Composition of the isomerization process products: comparison of the isomerization process simulation model with experimental data

| Component          | Process without adv.   |                                   | Process with deisopent. |                                |
|--------------------|------------------------|-----------------------------------|-------------------------|--------------------------------|
|                    | Exp. Data<br>mole frac | Simulation<br>model, mole<br>frac | Exp. data<br>mole frac  | Simulation model,<br>mole frac |
| Hydrogen           | 0.000                  | 0.000                             | 0.000                   | 0.000                          |
| Hyd. chloride      | 0.000                  | 0.000                             | 0.000                   | 0.000                          |
| Hyd. sulphide      | 0.000                  | 0.000                             | 0.000                   | 0.000                          |
| Methane            | 0.000                  | 0.001                             | 0.000                   | 0.008                          |
| Ethane             | 0.001                  | 0.001                             | 0.001                   | 0.001                          |
| Propane            | 0.002                  | 0.002                             | 0.002                   | 0.003                          |
| i-butane           | 0.006                  | 0.005                             | 0.006                   | 0.000                          |
| n-butane           | 0.005                  | 0.002                             | 0.000                   | 0.001                          |
| i-pentane          | 0.427                  | 0.424                             | 0.316                   | 0.324                          |
| n- pentane         | 0.221                  | 0.227                             | 0.164                   | 0.155                          |
| 2,2-dimethylbutane | 0.087                  | 0.087                             | 0.139                   | 0.129                          |
| 2,3-dimethylbutane | 0.035                  | 0.036                             | 0.054                   | 0.054                          |
| 2-methylpentane    | 0.101                  | 0.101                             | 0.153                   | 0.153                          |
| 3-methylpentane    | 0.055                  | 0.056                             | 0.084                   | 0.084                          |
| n-hexane           | 0.038                  | 0.038                             | 0.057                   | 0.057                          |
| Benzene            | 0.000                  | 0.000                             | 0.000                   | 0.000                          |
| Methylcyclopentane | 0.011                  | 0.011                             | 0.017                   | 0.017                          |
| Cyclohexane        | 0.009                  | 0.009                             | 0.013                   | 0.015                          |
| Total:             | 1.000                  | 1.000                             | 1.000                   | 1.000                          |

Table 5: Octane numbers

| Process flow                  | Research octane no (RON) | Motor octane no (MON) |
|-------------------------------|--------------------------|-----------------------|
| Feed                          | 68.6                     | 68.2                  |
| Izomerate                     |                          |                       |
| Process without advancement   | 79.4                     | 77.8                  |
| Process with molecular sieves | 88.9                     | 87.7                  |
| Process with deisopentimizer  | 79.9                     | 79.6                  |

Tablica 6: Flowrates of isomerate

| Isomerate                     | Flowrate, Std m <sup>3</sup> /h |
|-------------------------------|---------------------------------|
| Process without advancement   | 43.0                            |
| Process with molecular sieves | 42.8                            |
| Process with deisopentanizer  | 62.3                            |

In case of choosing the process with molecular sieves, apart from adding the molecular sieves, one must take into account also the change of operating conditions caused by the installation of the said process unit. Namely, by the recycle from molecular sieves, other process units are additionally burdened by increased flowrate, causing space velocity change in the reactor itself. Thus for instance the flowrate increase for the said reactor is as much as 42%. This is a considerable flowrate change, requiring the installation of a new reactor, which needs to be explored additionally. The impact on other process units must also be studied carefully.

On the other hand, the process using the feed with a reduced content of isopentane requires only an additional column with its marginal process equipment. This enables the processing of more low octane feed at the same plant. The mixing of product from the top of deisopentanizer with the process product, the isomerate, provides higher yield.

Therefore, the solution involving deisopentanizer seems simpler and more acceptable, but, since the main objective of oil refineries is the octane number increase, the solution involving molecular sieves must still be explored.

## 5.0. Conclusions

Based on the experimental data of the industrial process, we have set a simulation model of the reactor and the entire isomerization process, by applying the software for resolving the system of linear and non-linear equations Lingo, and the process simulation software ChemCad. Certain comparisons of different processes were performed with the purpose of improving the octane number and isomerate yield, all in view of advancing the quality of motor gasoline.

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

- By comparing experimental data with those of simulation models, one may observe changes of the isomerate composition with regard to the input feed, seen in increased mole fractions of iso-compounds (isopentane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane), as well as reduced mole fraction of n-pentane and n-hexane.
- The results of simulating the improved process by feed prefractionation in the deisopentanizer column have shown increase of the isomerate volumetric flow

by 45% with regard to the basic process. The accompanying RON value increase was very small.

- Process improvement by adding molecular sieves, enabling the return of straight-chained hydrocarbons into the feed, has resulted in the isomerase RON increase by 9 units at nearly the same isomerase flow, in comparison with the process without advancement.
- Results of simulating the implemented isomerization process variants have shown a very good match with the experimental data of the industrial process.
- The paper did not consider the economic aspects of the said improvements, but one may assume that the solution involving the deisopentanizer column would be more acceptable unless the achievement of very high RON values constitutes refinery priority. On the other hand, the process with molecular sieves requires additional process analysis and dimensioning of the process units and equipment.

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