Maja Fabulić Ruszkowski, Marko Radošević, Zoran Marić, Milorad Đukić, Zdenko Čulig, Štefica Podolski, Vlasta Srića, Sanda Telen, Sergej Stipaničev

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DESTILACIJA I ANALIZA NAFTI PRERAĐENIH U DOMAĆIM RAFINERIJAMA

Sažetak

U radu su okarakterizirana četiri uzorka nafti: domaća nafta i nafta REB (Russian export blend) koje se prerađuju u Rafineriji nafte Sisak, nafta Siberian Light koja se prerađuje u Rafineriji nafte Rijeka te nafta REB Odessa, Ukrajina, kao potencijalna nafta za preradu u RN Rijeka. Atmosferska i vakuum destilacija uzoraka nafti provedene su po ASTM D 2892 i ASTM D 5236 metodi.

Dobiven je niz podataka o fizikalnim i kemijskim svojstvima uzoraka nafti, destilaciji pravog vrelišta te iskorištenju i karakteristikama frakcija koje daju dovoljno informacija koje se mogu korisno upotrijebiti kod vrednovanja nafti (npr. izrada crude oil assay) i izbora preradbenih shema.

1. Uvod

Po kemijskom sastavu nafta je kompleksna smjesa ugljikovodika koja sadrži spojeve sumpora, dušika, kisika te metale. Fizikalno-kemijske karakteristike te iskorištenja i svojstva proizvoda koji se iz nje dobivaju razlikuju se od sirovine do sirovine, ovisno o tipu i koncentraciji ugljikovodika te udjelu heterogenih spojeva. Za ocjenu nafte kao potencijalne sirovine za preradu vrlo je važno upoznati se s njezinim fizikalno-kemijskim karakteristikama[1-4].

Podaci dobiveni destilacijom sirove nafte omogućuju procjenu prinosa i kvalitete produkata koji će biti dobiveni u preradi, prvenstveno goriva i motornih ulja, što se koristi za optimalni izbor nafte pri kupnji. Navedeni podaci mogu se koristiti i za projektiranje novih te izmjenu postojećih postrojenja. Također se može evaluirati vrijednost domaće nafte koja se redovito koristi u preradi.

Raspon vrelišta naftnih frakcija iz destilacijske kolone često se razlikuje i određuje se prema vrsti nafte i traženoj kvaliteti proizvoda. U tablici 1 pokazan je primjer broja C atoma u pojedinim naftnim frakcijama i raspon vrelišta frakcija [5].

2. Eksperimentalni dio

2.1 Ispitane sirovine

U radu su ispitane sljedeće sirove nafte: domaća nafta i nafta REB iz RN Sisak, nafta Siberian Light iz RN Rijeka i potencijalna nafta REB Odessa. U tablici 2 dane su osnovne karakteristike ispitivanih nafti.

Prema klasifikaciji nafte prema gustoći, domaća nafta ubraja se u lake nafte, dok su ostale tri nafte srednje gustoće. Prema sadržaju parafina sve četiri nafte su niskoparafinske s količinom parafina ispod 5,0 % m/m. Vrlo velika količina sumpora nađena je u nafti REB Odessa te ona predstavlja visoko sumpornu naftu, dok Siberian Light nafta predstavlja srednje sumpornu naftu. Domaća nafta sa znatno manjom količinom sumpora ubraja se u niskosumporne nafte.

Najveća količina Ni i V nađena je u REB nafti, dok domaća nafta sadrži još i Fe, Si, Al i Ca (tablica 3).

2.2 Metode ispitivanja

Za destilaciju nafte korištena je ASTM D 2892 standardna metoda za destilaciju sirove nafte (15 teoretskih tavana u koloni) [6]. Metoda se koristi za destilaciju stabilizirane nafte do temperature 400 °C AET (atmosferski ekvivalentne temperature) s frakcijskom kolonom i refluksnim omjerom 5:1. Rezultati se najčešće prikazuju u obliku destilacijske krivulje (ovisnost T o % m/m destiliranog produkta). Metoda destilacije naziva se TBP (eng. true boiling point – prava temperatura vrenja). Nakon atmosferske i vakuum destilacije do 400 °C na TBP uređaju, destilacija se nastavlja pod većim vakuumom na Potstill uređaju. Na Potstill uređaju koristi se ASTM D 5236 standardna test metoda za destilaciju teških ugljikovodičnih smjesa čija je temperatura vrenja viša od 150 °C. Metoda se koristi za destilaciju teške nafte, naftnih destilata, ostataka i sintetičkih smjesa [7]. Maksimalna ostvariva atmosferski ekvivalentna temperatura (AET) ovisi o vrijednosti topline smjese i u većini slučajeva dostiže 570 °C.

Proces destilacije uzoraka nafti započinje postupkom debutanizacije do 50 °C na TBP uređaju, a zatim se nastavlja destilacija do 390 °C, tj. do 570 °C na Potstill uređaju. Frakcije destilacije uzimane su svakih 20 °C i analizirane (sadržaj sumpora i ugljikovodični sastav). Također su napravljene i destilacije u kojima su dobivene sljedeće frakcije: primarni benzin (<80 °C), teški benzin (80-205 °C), petrolej (205-255 °C), LPU (255-345 °C), AO (>370 °C), TPU (345-455 °C), VPU (455-570 °C) i VO (>570 °C). Dobivenim frakcijama određen je sadržaj sumpora. Ispitane nafte uspoređene su na osnovi dobivene materijalne bilance i prinosa produkata.

2.3 Uređaj za TBP i Potstill destilaciju

Uređaji za destilaciju EuroDist System ASTM-D 2892, True Boiling Point i EuroDist System ASTM-D 5236, Potstill (Rofa, Njemačka) u potpunosti su automatizirani i posjeduju kontrolni sustav koji omogućuje praćenje i regulaciju procesa destilacije te bilježenje podataka mjerenjem pomoću EuroDist Control software. Parametri destilacije kao i veličina rezova mogu se mijenjati tijekom destilacije. Dobiveni rezovi automatski se važu te se dobiva destilacijski izvještaj u grafičkom i tabličnom obliku. TBP kolona s 15 teorijskih tavana odlikuje se dobrim odjeljivanjem komponenti u smjesi, odnosno nafti.

Euro Dist Control software jednostavan je za rukovanje, objedinjuje podatke iz TBP i Potstill destilacije u jedan izvještaj, što inače nije moguće napraviti s podacima dobivenim iz pojedinačnih TBP i Potstill destilacija. U tablici 4 dani su tehnički podaci za navedene uređaje. U navedenim uređajima moguće je dobiti dostatne količine pojedinih naftnih frakcija poput lakog i teškog benzina, dizelskog goriva koje se zatim mogu koristiti kao sirovine za ispitivanje u drugim procesima, npr. u procesu hidrodesulfurizacije. Također je moguće provesti i destilaciju smjesa poput uzoraka biodizelskog goriva, gdje je cilj destilacije samo čišćenje uzorka.

2.4 Ostale analize

Debutanizirani plin uzet prije početka destilacije na TBP uređaju analiziran je tehnikom plinske kromatografije pomoću ASTM 2427 metode.

Ugljikovodični sastav frakcija destilacije određen je tehnikom NMR spektrometrije. Sastav frakcija do 200 °C određen je metodom za određivanje sastava benzina ^{1}H NMR spektrometrijom, dok su sve ostale frakcije određene metodom za određivanje sastava srednjih destilata (220-500 °C) ^{1}H NMR spektrometrijom.

Sadržaj sumpora u frakcijama određen je metodom za određivanje sumpora u derivatima nafte pomoću WDX-ray spektrometra (HR EN ISO 20884 metoda).

3. Rezultati i rasprava

U tablici 5 prikazana je dobivena materijalna bilanca za destilirane nafte. Najviše je predestiliralo domaće nafte, zatim slijede nafta Siberian Light te REB i REB Odessa nafta. Najveći ostatak zabilježen je kod nafte REB Odessa, zatim REB nafte te Siberian Light. Najmanji ostatak zabilježen je kod domaće nafte s 10,36 % m/m.

U tablici 6 dani su prinosi pojedinih frakcija dobiveni iz TBP i Potstill destilacije. Uočava se da je najviše benzina (primarnog i teškog), kao i petroleja dobiveno iz domaće nafte. Slijede prinosi ovih produkata Siberian Light nafte te nafte REB i REB Odessa. Prinosi LPU i TPU približno su isti kod sve četiri nafte. Količina dobivenog VPU smanjila se korištenjem domaće nafte. Nafte Siberian Light i REB dale su slične prinose VPU, dok je iz nafte REB Odessa dobivena najveća količina VPU.

Na slici 1 prikazana je destilacijska krivulja dobivena iz podataka spojenih TBP i Potstill destilacija.

Debutanizirani plin analiziran je tehnikom plinske kromatografije. Iz sve četiri vrste nafte debutanizacijom je dobivena slična količina metana (od 0,31-0,41 % m/m), dok je iz domaće nafte dobiveno najviše etana. Veće količine propana ostvarene su s naftama Siberian Light i REB Odessa (slika 2).

Najveći prinos izobutana kao važne sirovine za proces alkilacije dobiven je iz domaće nafte, a najveći prinos n-butana dala je REB nafta. Prinos izopentana znatno je niži od ostalih C3-C4 komponenti ugljikovodika kod svih nafti. REB je ostvario oko 3 puta viši prinos izo-pentana od ostale tri ispitivane nafte (slika 3).

Ugljikovodični sastav frakcija benzina određen je tehnikom NMR spektrometrije. Iz slike 4 i 5 vidljivo je da količina parafina postupno pada s porastom temperature vrenja frakcija, dok količina aromata raste kod frakcija benzina dobivenog iz nafti Siberian Light, REB i REB Odessa. Kod domaće nafte u frakciji nakon 150 °C dolazi do ponovnog rasta parafina, tj. komplementarnog pada aromata. Količina aromata najveća je u frakcijama benzina dobivenog iz domaće nafte, koja je u ovom slučaju bila sastavljena od nafte Moslavina koja je bogata aromatskim ugljikovodicima.

Na slici 6 i 7 prikazan je sadržaj parafina i naftena te aromata u srednjim i teškim frakcijama. Uočava se da količina parafinskih i naftenskih ugljikovodika pada s porastom temperature vrenja, odnosno količina aromatskih ugljikovodika uglavnom raste. Frakcije dobivene iz domaće nafte imaju nešto više parafina i naftena te manju količinu aromatskih ugljikovodika čija količina varira s porastom temperature vrenja od frakcija dobivenih iz ostalih nafti.

Na slici 8 prikazan je sadržaj sumpora u pojedinim frakcijama dobivenim destilacijom nafte. Vidljivo je da je najveća koncentracija sumpora prisutna u naftama REB i REB Odessa, što je i trebalo očekivati s obzirom na početnu koncentraciju sumpora u tim naftama. Koncentracija sumpora u tim naftama počinje značajno rasti u frakcijama iznad 290 °C, da bi kod zadnje frakcije ta razlika iznosila gotovo 1 % m/m u odnosu na naftu Siberian Light, tj. gotovo 1,5 % m/m u odnosu na domaću naftu. U svim frakcijama domaće nafte nalazi se najmanja koncentracija sumpora, dok se u frakcijama Siberian Light nalazi nešto više sumpora od domaće nafte.

Koncentracije sumpora u pojedinim frakcijama dane su u tablici 7. Kod produkata nastalih iz domaće nafte sumpor počinje značajnije rasti u frakciji LPU. Produkti nastali iz nafte Siberian Light ne sadrže visoku koncentraciju sumpora, dok produkti nastali iz nafte REB, a posebice REB Odessa sadrže vrlo velik sadržaj sumpora koji je prisutan u težim frakcijama od LPU do VPU. Frakcije AO i VO nafti REB i REB Odessa sadrže znatnu količinu sumpora u odnosu na domaću naftu i Siberian Light.

4. Zaključci

Iz destilacijske krivulje dobivena je materijalna bilanca i prinosi pojedinih frakcija destiliranih nafti. Na osnovi tih podataka moguće je usporediti ispitane nafte te također provesti vrednovanje novih - potencijalnih nafti za preradu. Dobiveni podaci mogu se koristiti za optimiranje proizvodnje naših rafinerija.

Domaća nafta ostvarila je najbolju raspodjelu i prinos lakih produkata. Slijedi nafta Siberian Light, dok su nafte REB, a posebice REB Odessa nafte s velikom koncentracijom sumpora iz kojih se dobije manja količina benzina i petroleja, a veća količina VPU i ostatka.

Iz TBP i Potstill uređaja za destilaciju dobivaju se dostatne količine produkata zaprovođenje daljnjih poluindustrijskih ispitivanja, kao što su npr. hidroobrada teških benzina i srednjih frakcija.

Analitičke tehnike kojima su analizirane frakcije od velike su koristi pri detaljnoj karakterizaciji i davanju potpune slike o određenoj nafti.

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UDK	ključne riječi	key words
665.612.033	naftna sirovina, odnos sastava i procesnih svojstava	crude oil constituents to processing properties relation
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.002.33	gledište podobnosti sirovine za obradbu	process capability of feedstock
536.423.1	ispitivanje destilacijom	testing by distillation

Autori:

Maja Fabulić Ruszkowski[1], Marko Radošević[1], Zoran Marić[1], Milorad Đukić[2], Zdenko Čulig[2], Štefica Podolski[1], Vlasta Srića[1], Sanda Telen[1], Sergej Stipaničev[3]

[1]Sektor istraživanja i razvoja,Lovinčićeva bb,Zagreb, maja.fabulic-ruszkowski@ina.hr

[2] Rafinerija nafte Sisak, A. Kovačića 1, Sisak

[3] Rafinerija nafte Rijeka, Urinj bb, Kostrena

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Tablica 1: Primjer broja C atoma i raspona vrelišta naftnih frakcija iz destilacijske kolone
Table 1: Examples of C numbers and oil fraction's boiling point range from distillation's column

Naftna frakcija **Crude fraction**	**približan broj C atoma** **approx. number of C atom**	**približno vrelište, °C** **approx. boiling point, °C**
Atmosferska destilacija / Atmospheric distillation		
Laki plinovi/Light gases	C2-C4	-90 do 1
Benzin (laki, teški)/Naphtha (light,heavy)	C4-C10	1-200
Petrolej/Kerosene	C11-C14	205-255
Lako plinsko ulje/Light gas oil	C14-C18	255-315
Vakuum destilacija / Vacuum distillation		
Teško plinsko ulje/Heavy gas oil	C18-C28	315-425
Vakuum plinsko ulje/Vacuum gas oil	C28-C55	425-600
Ostatak/Bottom	>C55	600+

Tablica 2: Osnovne karakteristike ispitanih nafti
Table 2: Basic characteristics of using crudes

Karakteristike **Characteristics**	**Domaća** **Croatian**	**REB**	**Siberian** **Light**	**REB-** **Odessa**
Gustoća/Density, 15 °C, kg/dm^3, (ASTM D 5002)	0,8232	0,8775	0,8506	0,8728
°API (DMA 4500)	40,23	29,61	34,70	30,48
Voda/Water, % m/m(ASTM D 4006e1)	<0,5	<0,5	<0,5	<0,5
Tecište/Pour point ,°C (ASTM D 97)	Ispod -30	-4	-13	+8
Sumpor/Sulphur ,% m/m (HRN EN ISO 20884)	0,295	1,411	0,6320	1,573
Parafini/Parafines ,% m/m (UOP 46),	2,3	2,85	2,24	4,72
Viskoznost/Viscosity, 30 °C mPa s (ASTM D 445)	2,50	8,54	5,15	12,04
Viskoznost/Viscosity, 30 °C mm^2/s (ASTM D 445)	3,08	9,84	6,13	13,95
ASTM destilacija (ASTM D 86) Početak/Start, °C	52,0	41,9	56,1	41,4
Prinos/Yield 10 % v/v	98,0	135,9	130,8	140,8
20 % v/v	128,0	188,8	175,3	199,6
30 % v/v	160,0	242,7	225,20	254,9
40 % v/v	205,0	290,5	279,4	302,8
50 % v/v	255,0	336,0	325,3	344,1
60 % v/v	306,0	356,9	360,6	356,4
70 % v/v	355,0	-	373,7	-
75 % v/v	380,0	-	-	-
Kraj/End	383,0	360,5	373,7	356,4

Tablica 3: Količina metala u ispitanim naftama
Table 3: Metals in tested crudes

Metali **Metals mg/kg**	**Domaća** **Croatian**	**REB**	**Siberian Light**	**REB-Odessa**
Ni	26	39	36	28
V		86	26	76
Fe	32	23		
Si	300			
Al	230			
Ca	38			

Tablica 4: Tehnički podaci za uređaje EuroDist System ASTM-D 2892 - True Boiling Point i EuroDist System ASTM-D 5236-Potstill
Table 4: Technical data for apparatuses EuroDist System ASTM-D 2892 - True Boiling Point and EuroDist System ASTM-D 5236-Potstill

Karakteristike/Uređaj **Characteristics/Apparatus**	**EuroDist System** **ASTM-D 2892 -TBP**	**EuroDist System** **ASTM-D 5236- Potstill**
Najviša T tikvice, °C max. flask T, °C	400	400
Najviša AET temperatura, °C max. AET temperature, °C	420	600
Najviši radni tlak, Torr max. operation pressure, Torr	1	1-0,1
Volumen tikvice, l Flask volume, l	20	6
Volumen uzorka, l Sample volume, l	8-12	2-4
Volumen prihvatnih posuda, ml Receiver volume, ml	500 ili 1000	500 ili 1000
Najveći broj rezova, max. cuts	99	99

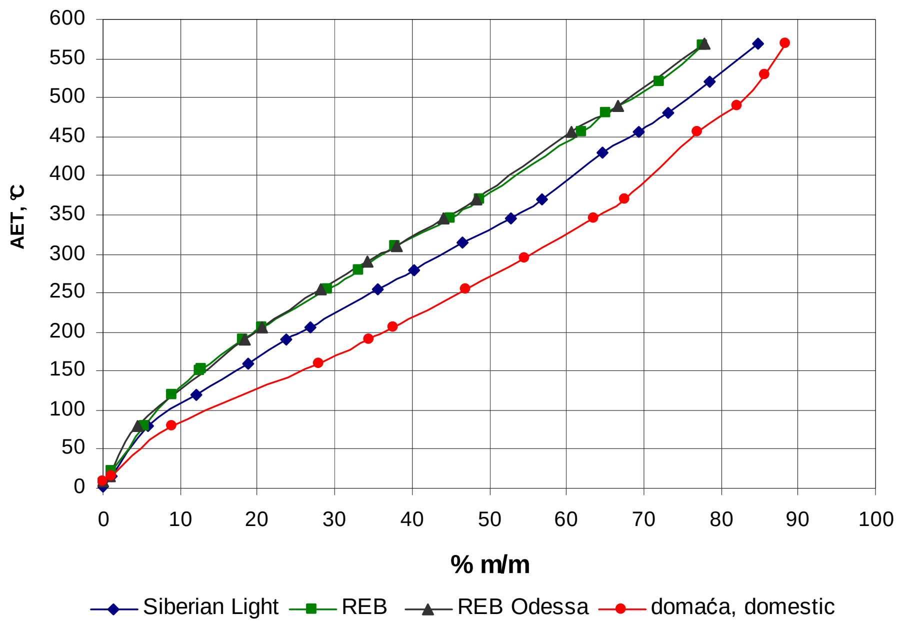
Tablica 5: Materijalna bilanca
Table 5: Material balance

Nafta **Crude**	**Domaća** **Croatian**	**REB**	**Siberian** **Light**	**REB** **Odessa**
Ukupni rezovi, % m/m Total cuts, % m/m	87,34	78,03	83,53	76,97
Plinska frakcija, % m/m Gas fraction, % m/m	1,08	1,06	1,16	0,80
Ostatak, % m/m Bottom, % m/m	10,36	19,51	14,53	20,72
Ukupno dobiveno, % m/m Total, % m/m	98,78	98,60	99,22	98,49

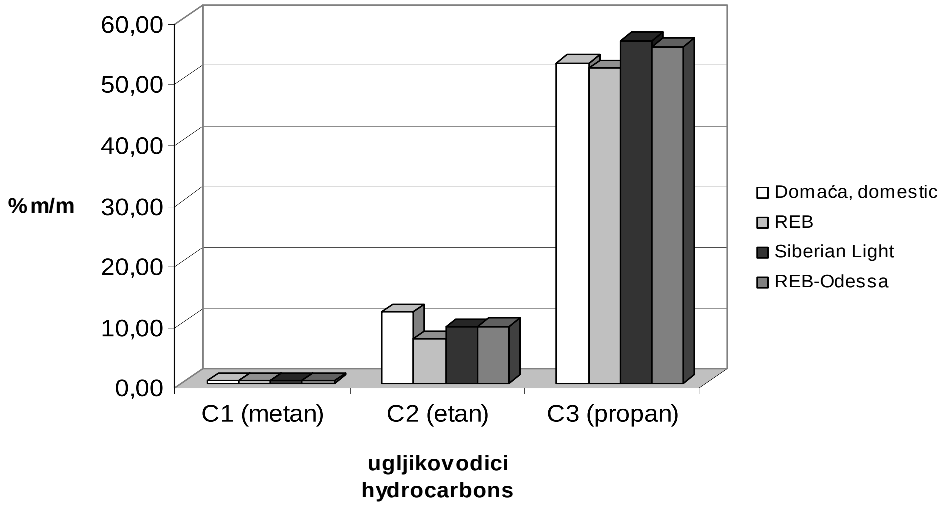
Tablica 6: Prinosi naftnih frakcija dobivenih iz TBP i Potstill destilacije
Table 6: Yields of crude fractions from TBP and Potstill distillation

Frakcija, % m/m Fraction, % m/m	Domaća Croatian	REB	Siberian Light	REB Odessa
Laki benzin (IBP-80 °C), Light naphtha	9,03	5,8	5,9	4,4
Teški benzin (80-205°C), Heavy naphtha	28,6	15,3	20,9	16,2
Petrolej (160-255 °C), Kerosene	9,5	8,6	8,8	7,7
LPU (255-345 °C), LGO	16,5	15,8	17,1	15,8
TPU (345-455 °C), HGO	13,5	16,9	16,7	16,6
VPU (455-570 °C), VGO	11,4	15,8	15,2	17,1

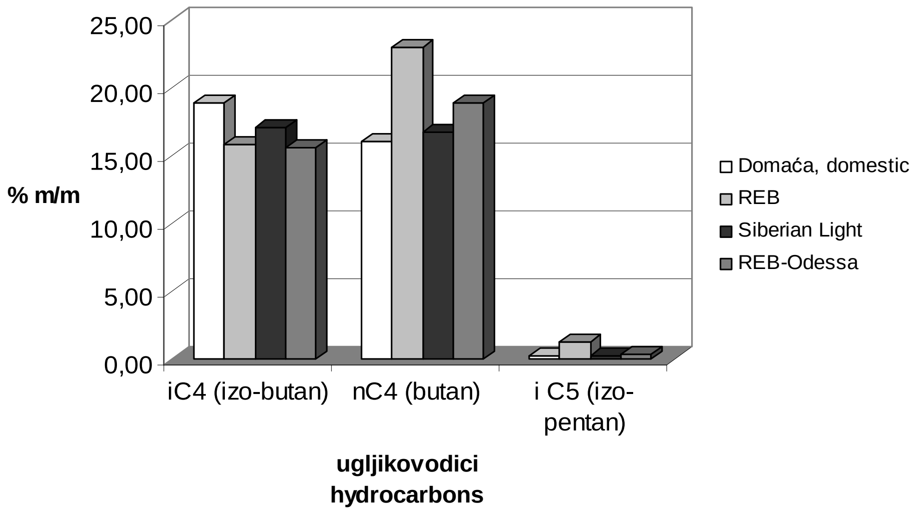
Slika 1: SpojeneTBP i vakuum destilacijske krivulje ispitivanih nafti
Figure 1: Merged TBP and vacuum distillation curve of crude oils



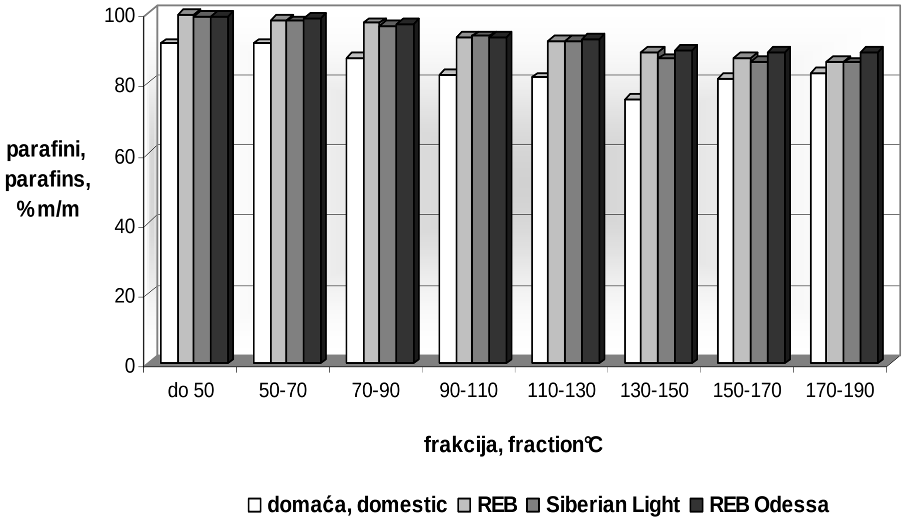
Slika 2: Udjeli C1-C3 u debutaniziranom plinu
Figure 2: C1-C3 share in debutanisation gas



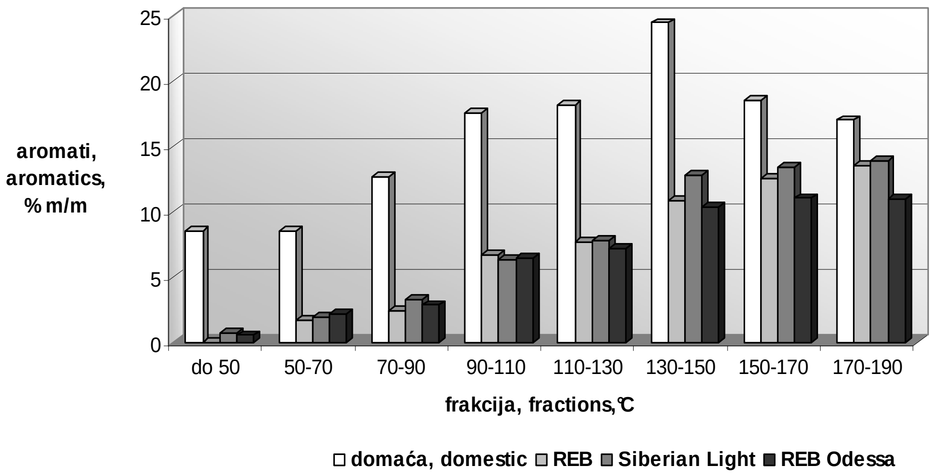
Slika 3: Udjeli C4-C5 u debutaniziranom plinu
Figure 3: C4-C5 share in debutanisation gas



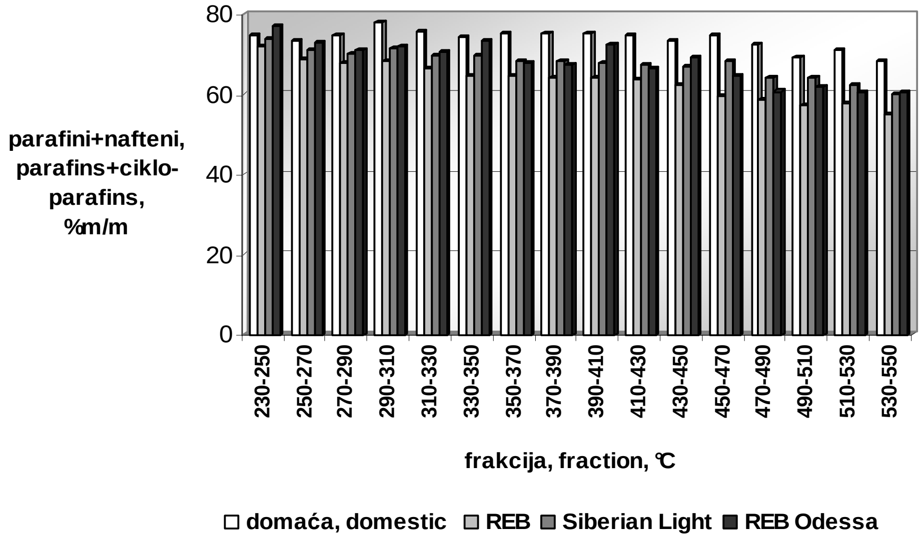
Slika 4: Udjel parafina u frakcijama benzina
Figure 4: Parafinic compounds share in gasoline fractions



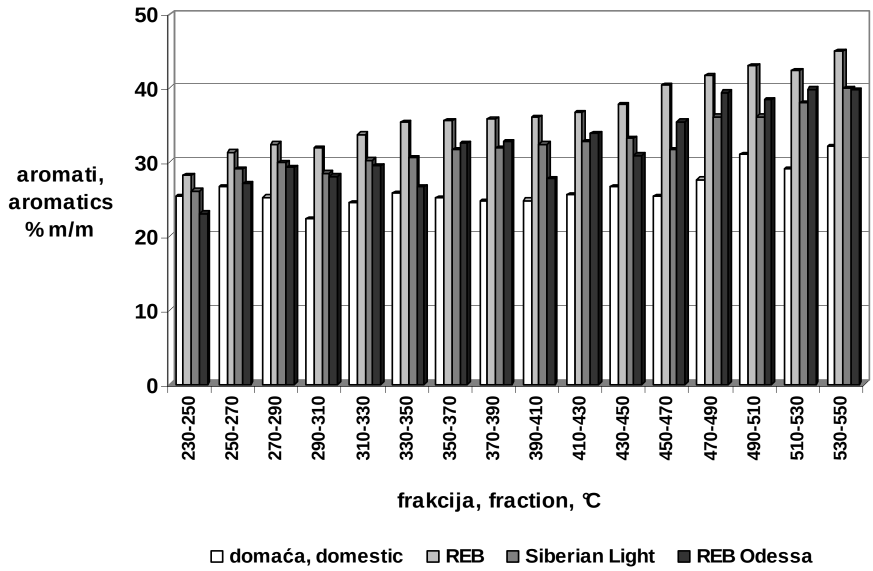
Slika 5: Udjel aromata u frakcijama benzina
Figure 5: Aromatic compounds share in gasoline fractions



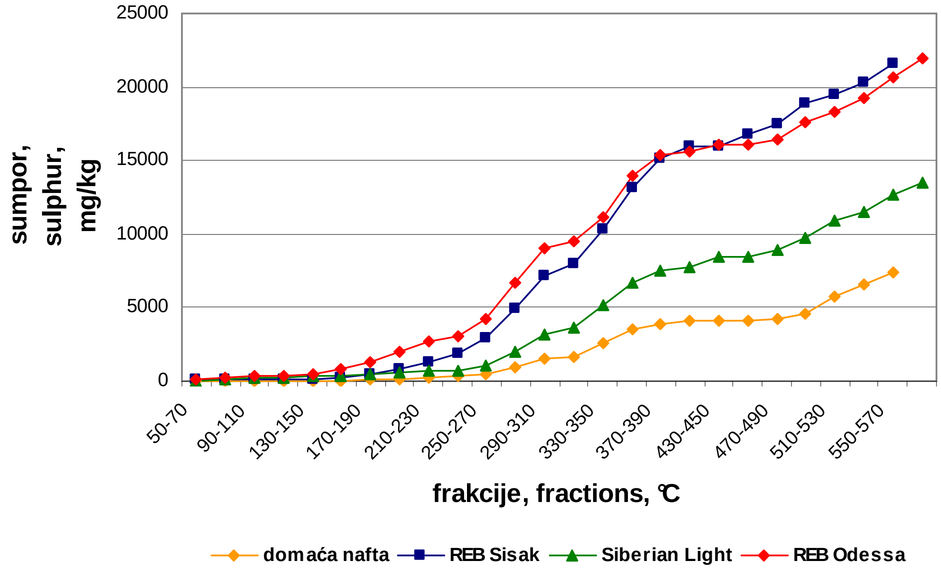
Slika 6: Udjel parafina i naftena u srednjim i teškim frakcijama
Figure 6: Parafinic and naphtenic compounds share in middle and heavy fractions



Slika 7: Udjel aromata u srednjim i teškim frakcijama
Figure 7: Aromatic compounds share in middle and heavy fractions



Slika 8: Sadržaj sumpora u pojedinim frakcijama ispitivanih nafti
Figure 8: Sulphur content in crude fractions



Tablica 7: Sadržaj sumpora u naftnim frakcijama
Table 7: Sulphur content in crude fractions

Sumpor **Sulphur**	**Domaća** **Croatian**	**REB**	**Siberian** **Light**	**REB** **Odessa**
Laki benzin (IBP-80 °C), mg/ kg Light naphtha	9	90	26	278
Teški benzin (80-205°C), mg/ kg Heavy naphtha	69	566	146	1318
Petrolej (205-255 °C), mg/ kg Kerosene	420	2610	792	3799
LPU (255-345 °C), % m/m LGO	0,193	0,860	0,387	1,109
AO (>370 °C), % m/m Atmosferic residue, % m/m	0,725	2,285	0,788	2,378
TPU (345-455 °C), % m/m HGO	0,408	1,582	1,171	1,640
VPU (455-590 °C), % m/m VGO	0,614	2,029	1,207	2,020
VO;(>590 °C) % m/m Vacuum residue, % m/m	1,154	2,841	1,771	2,910

Maja Fabulić Ruszkowski, Marko Radošević, Zoran Marić, Milorad Đukić, Zdenko Čulig, Štefica Podolski, Vlasta Srića, Sanda Telen, Sergej Stipaničev

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DISTILLATION AND ANALYSIS OF CRUDE OILS PROCESSED IN CROATIAN REFINERIES

Abstract

Characterisation of the four crude oil samples has been described in the paper: Croatian crude oil, REB (Russian export blend) crude oil processed at Sisak Oil Refinery, Siberian Light crude oil processed at Rijeka Oil Refinery, and potential REB Odessa crude oil. Atmospheric and vacuum distillations have been performed on the basis of ASTM D 2892 method for distillation of crude oil and its products, as well as on to the ASTM D 5236 method.

A series of data obtained on physical and chemical properties, true boiling point distillation, as well as utilisation and characteristics of fractions, provide enough information to be used in evaluation of crude oils (i.e. preparation of crude oil assay) and selection of process diagrams.

1. Introduction

According to its chemical composition, oil is a complex mixture of hydrocarbons, containing sulphur, nytrogen, and oxygen compounds, and metals. The physico-chemical properties, as well as yields and utilisation of products obtained from it, differ from one crude to another, depending on the type and concentration of hydrocarbons, as well as the share of heterogenous compounds. For evaluating oil as potential processing feed, it is extremely important to be familiar with its physico-chemical properties [1-4].

Data obtained by distillation of crude oil enable the estimation of the yield and quality of products primarily fuels and motor oils to be obtained in processing, which must be used for an optimal choice of crude at purchase. The said data may also be used for designing new, as well as alterating the existing plants. It is also possible to evaluate the value of Croatian crude regularly used in processing.

The range of boiling points of the oil fractions from distillation column is often different and is determined according to the type of crude and the required product quality. Table 1 presents an example of the number of C atoms in individual oil fractions, as well as the range of the fractions' boiling points [5].

2. The Experimental Part

2.1 The Feeds Tested

The following crudes were tested in the paper: Croatian crude and REB crude from the Sisak Refinery; Siberian Light crude from the Rijeka Refinery and potential crude REB Odessa. Table 2 provides the basic properties of the crudes tested.

According to the oil classification as per density, the local crude falls under light oils, while the remaining three crudes are of medium density. According to paraffin content, all four crudes are low-paraffin crudes with paraffin content below 5.0 % m/m. A very high sulphur content was found in the REB Odessa crude, so that it constitutes a high-sulphur crude, same as REB, while the Siberian Light constitutes a medium-sulphur crude. Croatian crude with a much lower sulphur volume pertains to low-sulphur oils.

The highest amount of Ni and V was found in the REB crude, while the local crude contains also Fe, Si, Al and Ca (Table 3).

2.2 The Methods Tested

For oil distillation, we have used the ASTM D 2892 standard test method for the distillation of crude oil (15 theoretical trays) [6]. The method is used for the distillation of stabilized oil up to the temperature of 400 °C AET (atmospheric equivalent temperature) with fractionating column and reflux ratio of 5:1. The results are presented mostly in the form of a distillation curve (dependence of T on the % m/m of distilled product). The method of distillation is called TBP (True Boiling Point). After atmospheric and vacuum distillation up to 400 °C on the TBP device, distillation is continued under a higher vacuum on the Potstill device. The Potstill device uses ASTM D 5236 standard test method for distillation of heavy hydrocarbon compounds whose boiling temperature is higher than 150 °C. The method is used for distillation of heavy crude oil, oil distillates, residues, and synthetic blends [7]. Maximum atmospheric equivalent temperature (AET) depends on the value of the blend's temperature and in most cases reaches 570 °C.

The process of distillation of oil samples begins with the procedure of debutanization of up to 50 °C on TBP device, followed by distillation up to 390 °C, i.e. up to 570 °C on Potstill device. Fractions of distillation were taken per every 20 °C and analyzed (sulphur content and hydrocarbon composition). Also performed were distillations providing the following fractions: naphtha (<80 °C), heavy gasoline (80-205 °C), kerosene (205-255 °C), LGO (255-345 °C), AR (>370 °C), HGOU (345-455 °C), VGO (455-570 °C) and VR (>570 °C). The obtained fractions were used to determine sulphur content. The tested crudes were compared based on the obtained material balance and product yield.

2.3 Device for TBP and Potstill Distillation

Devices for distillation EuroDist System ASTM-D 2892, True Boiling Point and EuroDist System ASTM-D 5236, Potstill (Rofa, Germany) are completely automatized and have a control system enabling the monitoring and regulation of the process of distillation, as well as data recording through measurement using EuroDist Control software. Parameters of distillation, as well as the size of cuts, may be changed during distillation. The cuts obtained are automatically weighed, obtaining distillation report in graphical and tabulary form. TBP column with 15 theoretical trays is characterized by good separation of components in the blend i.e. the crudes.

Euro Dist Control software is easy to handle, merging data from TBP and Potstill distillation into a single report, otherwise impossible with data obtained from individual TBP and Potstill distillations. Table 4 provides technical data for the said devices. The above devices provide sufficient volumes of individual oil fractions, such as light and heavy gasoline, diesel fuel, which may then be used as feed for testing in other processes, e.g. process of hydrodesulfurization. It is also possible to make distillation of compounds, such as samples of biodiesel fuel, the distillation goal being the sample cleaning itself.

2.4 Other Analyses

Debutanized gas taken before the beginning of distillation at TBP device was analyzed by the technique of gas chromatography, using the ASTM 2427 method.

The hydrocarbon composition of the fractions of distillation was determined using of NMR spectrometry. The fraction composition up to 200 ℃ was determined using the method for determining gasoline composition using ^{1}H NMR spectrometry, whereas all other fractions are determined by the method for determining the composition of medium distillates (220-500 ℃) ^{1}H NMR spectrometry.

Sulphur content in fractions was determined by the method for determining sulphur in oil derivatives using WDX-ray spectrometer (HR EN ISO 20884 method).

3. Results and Discussion

Table 5 presents the obtained material balance for distilled oils. It may be observed that the highest distillation amount was that of Croatian crude, followed by Siberian Light, REB and finally REB Odessa crudes. The largest residue was recorded for REB Odessa, followed by REB and Siberian Ligh crudes. The lowest residue was recorded for Croatian crude with 10.36 % m/m.

Table 6 provides yields of individual fractions obtained from TBP and Potstill distillation. It may be observed that the most gasoline (both naphtha and heavy g.), as well as kerosene, was obtained from Croatian crude. It is followed by the yields of the following products: Siberian Light crude, and REB and REB Odessa crudes. Yields of LGO and HGO are approximately the same for all the four crudes. The amount of obtained HGO was decreased by the use of Croatian crude. Crudes

Siberian Light and REB yielded aproximately the same amounts as VGO, while the REB Odessa crude provided the highest amount of VGO.

Figure 1 presents the distillation curve obtained from the merged data of TBP and Potstill distillations.

Debutanized gas was analyzed using the technique of gas chromatography. All the four crudes have through debutanization yielded a similar volume of methane (from 0.31-0.41 % m/m), while Croatian crude yielded the most ethane. Larger propane volumes were obtained using Siberian Light and REB Odessa crudes (Figure 2).

The highest yield of iso-butane, as an important feed for the process of alkylation, was obtained from Croatian crude, while the highest yield of n-butane was provided by REB crude. The yield of iso-pentane is much lower than that of other C3-C4 components for all crudes. REB has achieved approximately 3 times higher yield of iso-pentane than the other three tested crudes (Figure 3).

Hydrocarbon composition of gasoline fractions was determined using the technique of NMR spectrometry. Figures 4 and 5 reveal that the amount of kerosene gradually reduces with the increase of the boiling temperature of fractions, while the amount of aromatics increases for the fractions of gasoline obtained from crudes Siberian Light, REB and REB Odessa. In case of Croatian crude, in fraction above 150 °C there occurs a repeated kerosene growth i.e. a complementary aromatics decrease. The volume of aromatics is the highest in fractions of gasoline obtained from Croatian crude, because Croatian crude was in this case compounded of Moslavina crude, rich in aromatic hydrocarbons.

Figures 6 and 7 show the content of paraffinic, naphthene and aromatics in medium and heavy fractions. It may be observed that the volume of paraffinic and naphthenic hydrocarbons decreases with the increase of boiling temperature whereas the amount of aromatic hydrocarbons mostly increases. Fractions obtained from Croatian crude have somewhat more paraffins and naphthenics and a lower amount of aromatic hydrocarbons, whose volume varies with the increase of boiling temperature from fractions obtained from other crudes.

Figure 8 shows sulphur content per individual fractions obtained by oil distillation. It may be observed that the highest concentration of sulphur is present in crudes REB and REB Odessa, which was to be expected, given the initial concentration of sulphur in these crudes. The concentration of sulphur in these crudes begins growing considerably in fractions above 290 °C, while in the last fraction the difference amounts to almost 1 % m/m with regard to Siberian Light crude i.e. nearly 1.5 % m/m with regard to Croatian crude. In all fractions of Croatian crude there is the lowest concentration of sulphur, while the fractions of Siberian Light contain somewhat more sulphur than Croatian crude.

Concentrations of sulphur in individual oil fractions are provided in Table 7. With products obtained from Croatian crude, the sulphur starts increasing more considerably in LGO fraction. Products obtained from the Siberian Light crude do not contain a high concentration of sulphur, while products obtained from the REB crude, and particularly the REB Odessa, contain a very high sulphur content, present in heavier fractions from LGO to VGO. Fractions of AR and VR crudes REB and REB Odessa, contain a considerable volume of sulphur with regard to Croatian crude and the Siberian Light crude.

4. Conclusions

Distillation curve has provided the material balance and yields of individual fractions of distillied crudes. Based on these data, it is possible to compare the tested crudes and also evaluate new – potential crudes for processing. The obtained data may be used for optimizing the production of Croatian refineries.

Croatian crude has provided the best distribution and yield of light products. It is followed by the Siberian Light crude, while REB, and particularly REB Odessa, are crudes with a high concentration of sulphur providing a lower volume of gasoline and kerosene, and a higher volume of VGO and residues.

TBP and Potstill distillation devices provide sufficient volumes of products for performing further semi-industrial tests, such as e.g. hydrotreatment of heavy gasoline and medium fractions.

Analytical techniques used for analyzing fractions are of great use for a detailed characterization and providing of a complete insight of a tested crude.

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UDK	ključne riječi	key words
665.612.033	naftna sirovina, odnos sastava i procesnih svojstava	crude oil constituents to processing properties relation
.002.33	gledište izbora i predobrade sirovina	raw materials choice and pretreatment viewpoint
.002.33	gledište podobnosti sirovine za obradbu	process capability of feedstock
536.423.1	ispitivanje destilacijom	testing by distillation

Authors:
Maja Fabulić Ruszkowski[1], Marko Radošević[1], Zoran Marić[1], Milorad Đukić[2], Zdenko Čulig[2], Štefica Podolski[1], Vlasta Srića[1], Sanda Telen[1], Sergej Stipaničev[3]
[1]INA Sektor istraživanja i razvoja, Lovinčićeva bb, Zagreb, maja.fabulic-ruszkowski@ina.hr
[2] INA Rafinerija nafte Sisak, A. Kovačića 1, Sisak
[3] INA Rafinerija nafte Rijeka, Urinj bb, Kostrena

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