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SEPARACIJA I KROMATOGRAFSKA ANALIZA PLINSKOG ULJA

Sažetak

Poznavanje detaljnog ugljikovodičnog sastava plinskog ulja dobivenog iz visbreaking procesa, koji se koristi za umješavanje u dizelsko gorivo, važno je za predviđanje kvalitete i ekoloških svojstava krajnjeg komercijalnog produkta. Plinsko ulje je kompleksna smjesa različitih grupa ugljikovodika: parafina, naftena, olefina, aromata, polarnih spojeva. Njihov ukupni sadržaj i međusobni odnos diktiraju konačna primjenska i ekološka svojstva. Za određivanje ugljikovodičnog sastava često se primjenjuju instrumentalne analitičke tehnike, među kojima dominiraju različite kromatografske tehnike (HPLC, GC, GC/MS, TC). Potpuna separacija ugljikovodičnih grupa vrlo se teško postiže zbog broja komponenata u pojedinoj grupi kao i zbog njihovog strukturnog sastava. Predfrakcionacijom plinskog ulja HPLC tehnikom na silikagel koloni modificiranoj srebrnim ionima, zasićeni ugljikovodici separirani su od ukupnih nezasićenih ugljikovodičnih grupa. Separirane frakcije analizirane su dalje tekućinskom kromatografijom visoke djelotvornosti normalnih faza (NP HPLC) uz detekciju na UV/DAD detektoru.

Uvod

Proces visbreakinga (smanjenje viskoznosti ili lom vikoznosti) blaži je oblik toplinskog krekiranja koji se provodi s ciljem smanjenja i ujednačavanja viskoznosti i smanjenja stišta loživom ulju. Dobiva se i do 20 % hlapljivih proizvoda, posebice plinska i benzinska frakcija i lako plinsko ulje. [1] Sirovina za visbreaking, ostatak atmosferske destilacije i teško plinsko ulje, odlazi u striper kolonu gdje se pomoću vodene pare uklanjaju lagane komponente kako bi se dobila željena kvaliteta plinskog ulja. Nakon stripera plinsko ulje ide na hidroobradu radi uklanjanja sumpornih spojeva i zasićenja olefinima. Vakuum plinska ulja s visbreakinga šalju se kao sirovina na blagi hidrokreking ili uz prethodnu hidroobradu na FCC proces. Benzin i plinsko ulje moraju proći hidroobradu da bi se mogli namiješati u motorne benzine, dizelsko gorivo ili loživo ulje za domaćinstvo.

Karakteristika plinskog ulja kao i sirove nafte te naftnih produkata je složeni ugljikovodični sastav. Sastav i prisutnost određenih specifičnih ugljikovodičnih skupina u nekom produktu ovisi o vrsti produkta i o postupku procesne obrade. Kako

bi se predvidjeli potencijali goriva ili odredili zahtjevi za poboljšanjem kvalitete, neophodno je poznavanje kemijskih svojstava goriva i prekursora goriva. Za karakterizaciju naftnih i srodnih produkata korištene su mnoge kromatografske tehnike.[2,3] U nekim slučajevima te su tehnike primijenjene za odvajanje i kvalitativno i kvantitativno određivanje pojedinih komponenti. No, kako primjenska svojstva većine fosilnih goriva i ulja ovise prije o određenoj kemijskoj grupi nego o pojedinim spojevima, korisno je kromatografsko određivanje grupnog sastava ugljikovodika prema nekom specifičnom svojstvu: polarnosti, aromatičnosti, broju C atoma i sl. Analizom grupnog sastava ugljikovodika može se odrediti kvaliteta goriva ili ulja, definirati varijable konverzijskih procesa, razjasniti reakcijski putovi i kinetika petrokemijskih reakcija te dobiti uvid u mogućnost prerade sirovine ili kvalitetu konačnog produkta. Kako bi bila idealna, kromatografska metoda za određivanje pojedinih spojeva, grupnog sastava ili distribucije vrelišta mora zadovoljiti sljedeće zahtjeve: mora biti točna i reproducibilna, brza, adekvatna za kontrolu kvalitete, kvalitativna i primjenjiva na sve uzorke uz što manje zahtjeve za dodatnom frakcionacijom. No, u slučaju teških frakcija naftnih uzoraka te za uzorke koji pokrivaju široko područje vrelišta i područja polarnosti, trenutačno dostupne kromatografske metode često imaju određena ograničenja. Obično problemi proizlaze iz neadekvatne moći otapanja, slabe hlapljivosti, slabe topljivosti komponenata uzorka na stacionarnoj fazi, jake apsorpcije komponenata uzorka na stacionarnoj fazi ili niske osjetljivosti detektora.

Vrlo često se pri analizama koristi istovremeno i više kromatografskih tehnika uz različite detekcijske sustave kako bi i separacija i identifikacija komponenata bila što efikasnija. U radu je prikazana analiza plinskog ulja dvostupnjevitom kromatografskom analizom. Prvi stupanj je predfrakcionacija na srebrom modificiranoj silikagel koloni, pripremljenoj u laboratoriju, a u kojem se separiraju zasićene (parafini, izoparafini i nafteni) od nezasićenih (olefini, aromati, heterociklički spojevi) frakcija. Srebrni ioni ulaze u reakciju s π-elektronima iz dvostrukih i višestrukih veza tvoreći polarne komplekse. Na taj se način svi spojevi i grupe spojeva koji u strukturi imaju nezasićenje zadržavaju na koloni duže od spojeva bez nezasićenja. Predfrakcionacijski korak razvijen je kako bi se unaprijedila detaljna grupna analiza ugljikovodičnih grupa u složenim naftnim produktima.[4] U drugom stupnju obje frakcije, zasićena i nezasićena, analizirane su tekućinskom kromatografijom visoke djelotvornosti normalnih faza (NP HPLC) uz detekciju UV detektorom polja dioda (UV/DAD).

Eksperimentalni dio

1.Predfrakcionacija

Predfrakcionacija plinskog ulja izvedena je na tekućinskom kromatografu tvrtke Agilent 1100, na μ-Porasil koloni (Waters). Za ova ispitivanja, silikagel kolona je modificirana srebrnim ionima. Kroz kolonu je propuštana vodena otopina srebrnog nitrata do zasićenja kolone. Nakon zasićenja kolone, kroz kolonu je propuštan n-heksan, pokretna faza u daljnjim frakcionacijskim analizama. Mijenjanjem brzine

protoka pokretne faze ispitala se promjena razlučivanja (R) kolone. Povećanjem razlučivanja kolone željelo se postići bolje razdvajanje ugljikovodičnih frakcija.

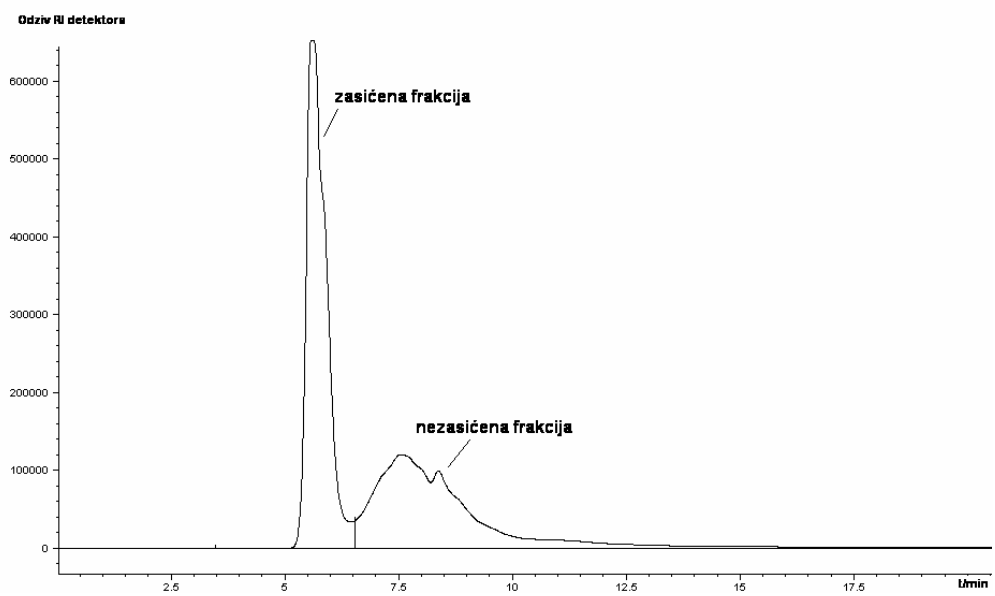
Tablica 1: Ovisnost razlučivanja kolone o brzini protoka mobilne faze

Brzina protoka (mL/min)	Razlučivanje
0,6	1,44
0,8	1,27
1,0	1,27

Iz tablice 1 vidljivo je da je razlučivanje kolone najveće kod protoka od 0,6 mL/min te je taj protok odabran kao radni. Vrijeme trajanja analize je 22,0 min jer je u tom vremenu eluiranje frakcija s kolone potpuno. Uzorak plinskog ulja otopljen je u n-heksanu i profiltriran kroz membranski mikrofiltar (Milipore) poroznosti 0,45 μm. Nakon pripreme, uzorak je injektiran na kolonu te su separirane zasićena i nezasićena ugljikovodična frakcija. Nakon separacije, sakupljene frakcije analizirane su NP HPLC metodom.

2. NP HPLC analiza

Frakcije separirane na srebrom modificiranoj silikagel koloni (slika 1) analizirane su na tekućinskom kromatografu tvrtke Varian.



Slika 1: Predfrakcionacija plinskog ulja na srebrom modificiranoj silikagel koloni

Instrument na kojem su izvedene NP HPLC analize, sastoji se od sljedećih modula:

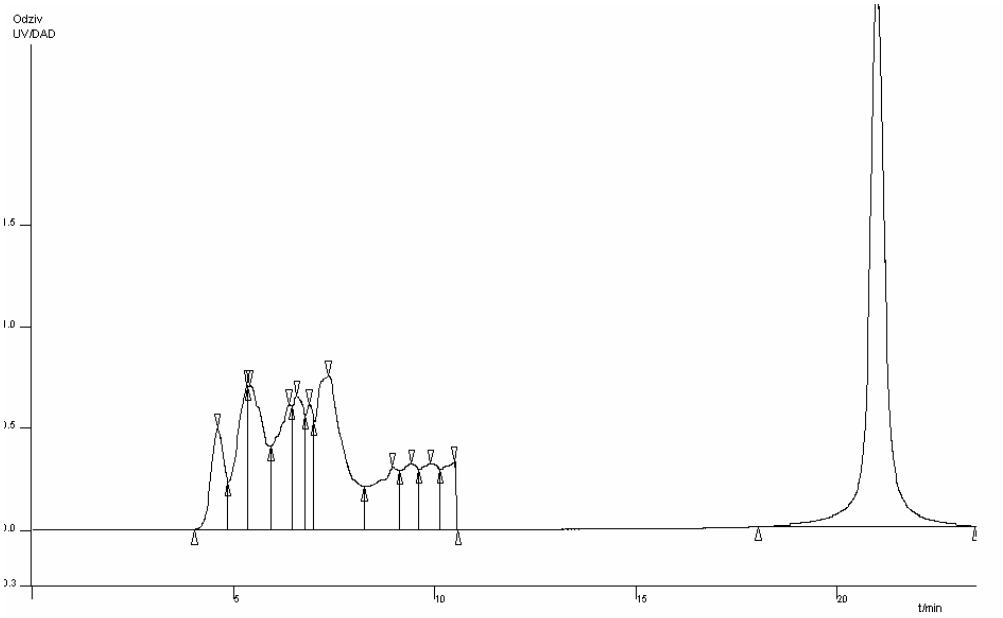
– visokotlačna pumpa (Varian 9012 Q)
– autosampler (ProStar 410, Varian)
– NH_2 analitička HPLC kolona, (Zorbax, Agilent, 4,6x250 mm, 5 µm)
– UV/DAD detektor (Varian 9065)

Radni uvjeti NP HPLC analiza bili su slijedeći:

mobilna faza	n-heptan, kromatografske čistoće (mobilna faza se otplinjava helijem)
brzina mobilne faze	0.8 ml/min
trajanje analize	22.5 min
temperatura kolone	27 ºC

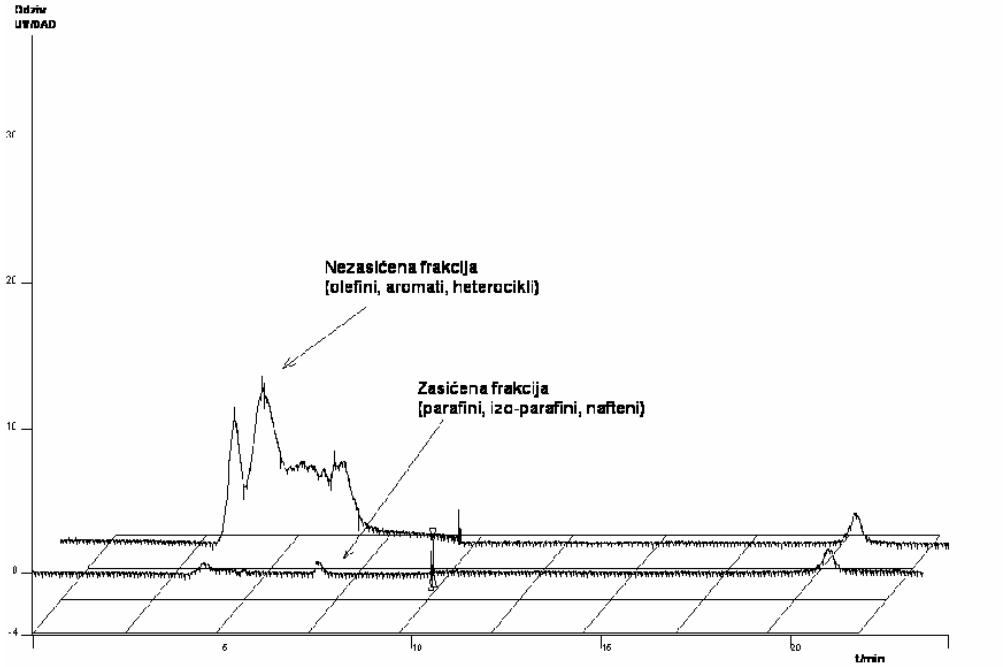
Rezultati i rasprava

Plinsko ulje separirano je na srebrom modificiranoj silkagel koloni na zasićenu i nezasićenu ugljikovodičnu frakciju. Jasno odijeljene frakcije vidljive su iz kromatograma (slika 1) kojim je praćen separacijski proces.



Slika 2: NP-HPLC kromatogrami plinskog ulja

NP HPLC metodom analizirano je cijelo plinsko ulje, koje nije podvrgnuto separaciji i iz njegovog kromatograma (slika 2) jasno je vidljivo da se radi o složenoj ugljikovodičnoj smjesi.Zasićena i nezasićena ugljikovodična frakcija analizirane su kromatografski i kvalitativno su određeni grupni sastavi obje frakcije (slika 3).

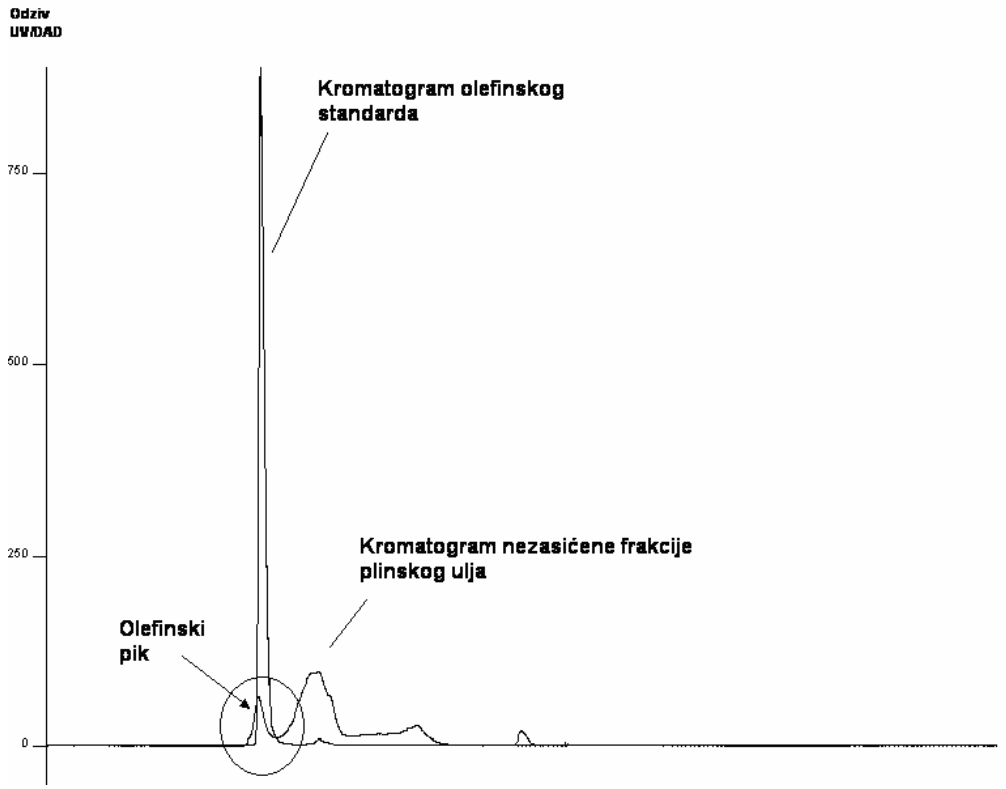


Slika 3: NP HPLC kromatogrami zasićene i nezasićene frakcije plinskog ulja

Usporedbom kromatograma uočava se da su u zasićenoj frakciji nezasićenja prisutna u tragovima. Time je potvrđeno da je stupanj separacije zasićenih od nezasićenih ugljikovodičnih grupa na srebrnoj koloni bio vrlo visok.

Prisutnost olefinskih ugljikovodika u nezasićenoj frakciji potvrđena je usporedbom kromatograma nezasićene frakcije s kromatogramom olefinskog standarda (slika 4). Stoga se ovakvim analitičkim pristupom rješava problem koeluiranja zasićenih i olefinskih frakcija kod NP HPLC analiza, na amino modificiranoj silikagel koloni.

Problem prikazane metode frakiconacije je u tome što je zbog dimenzija srebrne kolone (analitička kolona, veličina čestica punila je 10 µm) moguća frakcionacija kvantitativno male početne količine uzorka plinskog ulja, a frakcionacija je ponavljana nekoliko puta kako bi se nakon uklanjanja otapala dobila dovoljna količina pojedinih frakcija za daljnju analizu. To značajno otežava mogućnost kvantifikacije pojedinih ugljikovodičnih grupa koja bi također bila poželjna. U daljnjem radu planira se rad na preparativnoj kromatografskoj koloni većih dimenzija čestica punila, što bi omogućilo i veću početnu količinu analiziranog uzorka. Osim NP HPLC metodom separirane ugljikovodične frakcije mogu se dalje analizirati na drugim analitičkim tehnikama (pr. GC, GCxMS, GCxGC, NMR i sl.), na kojima je inače kvalitativna i kvantitativna analiza otežana zbog složenog sastava.



Slika 4: NP HPLC kromatogrami olefinskog standarda i nezasićene frakcije plin. ulja

Zaključak

U radu je prikazana dvostupnjevita tekućinsko kromatografska analiza plinskog ulja. U predfrakcionacijskom stupnju, na srebrom modificiranoj silikagel koloni, separirana je zasićena od nezasićene ugljikovodične frakcije. Čistoća frakcija potvrđena je daljnjom NP HPLC analizom. U NP HPLC kromatogramu zasićene frakcije, nezasićenja su prisutna u tragovima. Prisutnost olefinskih ugljikovodika u nezasićenoj frakciji potvrđena je uspoređivanjem kromatograma nezasićene frakcije plinskog ulja s olefinskim standardom. Daljnji rad potreban je na kvantifikaciji separiranih grupa, kako bi se dobio još potpuniji uvid u ugljikovodični sastav plinskog ulja.

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UDK	ključne riječi	key words
665.642.2	frakcija plinskog ulja visbreakinga	visbreaking gasoil
665.642.2.033.24	separacija olefina i parafina	olefine parafine separation
66.017	odnos sastava i svojstava	content to properties relation
543.544.5.068.7	tekućinska kromatografija visoke razlučivosti HPLC	high performance liquid chromatography HPLC
543.544-414	stacionarna faza u kromatografiji, Ag-silikagel	stationary phase in chromatography
543.544.5.068.7	UV/DAD spektrometrija nizom detektorskih dioda	UV/DAD Ultra violet diode array detection spectrometry

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SEPARATION AND CHROMATOGRAPHIC ANALYSIS OF GAS OIL

Abstract
Knowing the detailed hydrocarbon composition of the gas oil from visbreaking process used for blending of diesel fuel is very important for foreseeing the final commercial product quality and its ecological properties. Gas oil is complex mixture of different hydrocarbon groups: paraffines, naphtenes, olefins, aromatics, polar compounds. Their total content and relation control final product ecological and quality properties. Different chromatographic techniques (HPLC, GC, GC/MS, TLC) were used for determination of hydrocarbon composition in oil products. Complete hydrocarbon group separation is hard to reach because of the numerous components in one specific group and complex structure composition.
HPLC prefractionation step of gas oil was performed on the in-house made silver – modified silica gel column. On silver column unsaturated hydrocarbons retain longer than saturated due to double-bond π electrons. By fractionation saturated and unsaturated fraction was separated and further analysed by normal – phase high performance liquid chromatography hyphenated by UV/DAD detection.

Introduction

The visbreaking process (viscosity reduction or breaking) is a more moderate form of thermal cracking which is performed to reduce and equalize the viscosity and to reduce the pour point of fuel oil. In this process to 20 % of volatile products is produced, especially gas and gasoline fraction and light gas oil. [1] The raw material for the visbreaking, the residue of atmospheric destillation and heavy gas oil, enters a stripping column where water vapour removes the light components in order to achieve the desired quality of gas oil. After stripping gas oil is hydrotreated due to removing sulphur compounds and olefin saturation. Visbroken vacuum gas oil is, as the raw material, sent to be hydrocracked or sumitted to the FCC process (after being hydrotreated). Gasoline and gas oil have to be hydrotreated in order to blend into motor petrol, diesel fuel or fuel oil for the household consumption.
A complex hydrocarbon composition is a characteristic of gas oil, crude oil and oil products. The content and the presence of certain specific hydrocarbon groups in a product depends on its type and procedure of the process of treatment. To foresee

the fuel potentials or determine the requirements for the quality improvement we necessarily need to know the chemical properties of fuel and fuel precursor. For the characterization of petroleum and related products many chromatographic techniques were used. [2,3] In some cases these techniques were used for the separation and the quality and quantity determination of the components. Nevertheless, since the application properties of the most of fossil fuels and oils depend on the chemical group rather than on the specific compounds, it is usefull to perform a chromatographic determination of hydrocarbon group composition according to a specific property, such as polarity, aromaticity, the number of carbon atoms and the like. The analysis of the hydrocarbon group composition can determine the quality of fuel or oil, define the variables of conversion processes, explain the reaction paths and the kinetics of petrochemical reactions and provide an insight into the possibility of a raw material treatment process or the quality of the final product. To be ideal, the chromatographic method for the determination of specific compounds, group compositions and boiling point distribution has to meet the following requirements: it has to be correct and reproducible, fast, adequate for the quality control, qualitative and applicable for all the samples with as less requirements for the additional fractionation as possible. But the currently available chromatographic methods are often limited in cases of heavy fractions of petroleum samples and the samples covering a broad scope of boiling points and polarity. There are usually problems arising from inadequate solvation capability, low volatility of the sample components in the stationary phase, strong absorption of the sample components in the stationary phase or low detection sensibility.

To make the separation and the component identification as efficient as possible very often the analyses simultaneously include several chromatographic techniques with different detection systems. The paper shows the analysis of gas oil by two step chromatographic analysis. The first step is a prefractionation on a silver modified silica gel column which was prepared in a laboratory and on which saturated (paraffins, iso-paraffins and naphtenes) from unsaturated fractions (olefines, aromates, heterocyclic compounds) were separated. Silver ions enter the reaction with π-electrons from double and multiple bonds by forming polar complexes. In this way all the compounds and groups of compounds which are unsaturated in the structure remain on the column longer than saturated compounds. The prefractionation step was developed to improve the detailed group analysis of hydrocarbon groups in complex petroleum products [4]. In the second step both fractions were analysed by the normal phase high performance liquid chromatography (NP HPLC) hyphenated by the UV/DAD detection.

Experimental part

1.Prefractionation

The prefractionation of gas oil was performed on an Agilent 1100 liquid chromatograph using a μ-Porasil column (Waters). For the purpose of these examinations silica gel column was modified by the silver ions. Aqueous silver

nitrate solution through the column was passed till the column was saturated. After that, n-hexane was passed through the column. N-hexane served as a mobile phase in the further fractionation analyses. The change of a resolution column (R) was tested by changing of the flow rate of mobile phases. The intention of increasing the resolution column was to achieve better separation of hydrocarbon fractions.

Table 1: Dependence of column resolution on the flow rate of the mobile phase

Flow rate (mL/min)	Resolution
0,6	1,44
0,8	1,27
1,0	1,27

The Table 1 shows that the maximum value of the column resolution is at the flow rate of 0,6 mL/min and therefore this flow was chosen to be the operating one. The analysis lasted for 22,0 min since during this time the fraction eluation on a column was complete. A sample of gas oil was dissolved in n-hexane and filtrated through a membrane microfilter (Milipore) of the 0,45 μm pore size. After the preparation, the sample was injected on the column and the saturated and unsaturated hydrogen fractions were separated. After the separation the collected fractions were analysed by the NP HPLC method.

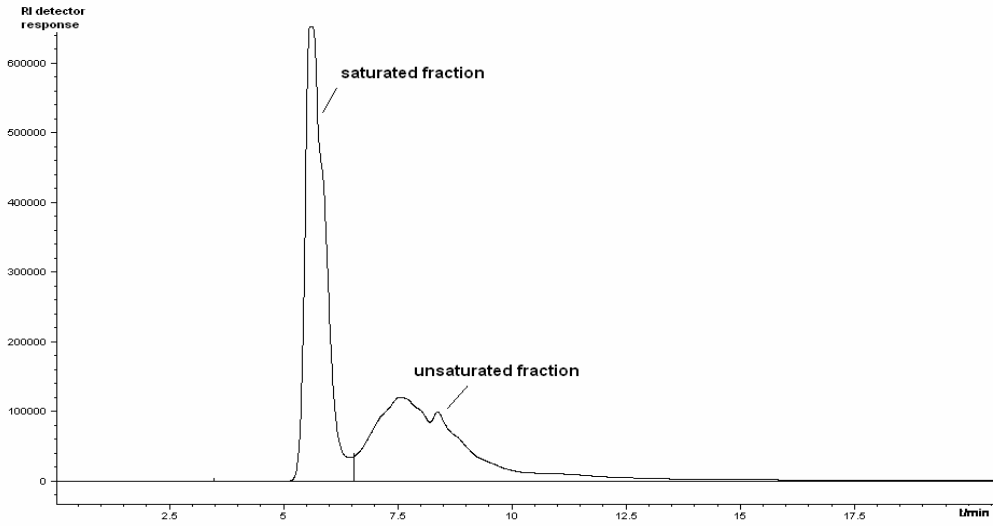

Figure 1: Prefractionation of gas oil on silver-modified silica gel column.

2. NP HPLC analysis

The fractions separated on the silver-modified silica gel column (Figure 1) were analysed on the liquid chromatograph from Varian, Inc.

The instrument used in the NP HPLC analysis consists of the following modules:

– Hifh pressure pump (Varian 9012 Q)
– Autosampler (ProStar 410, Varian)
– NH_2 analytical HPLC column, (Zorbax, Agilent, 4,6x250 mm, 5 µm)
– UV/DAD detector (Varian 9065)

The operating conditions of the NP HPLC analyses were as follows:

mobile phase	n-heptane, chromatographically pure (the mobile phase was degassed by helium)
mobile phase rate	0.8 ml/min
duration of analysis	22.5 min
column temperature	27 ºC

Results and discussion

Gas oil was separated on the silver-modified silica gel column into saturated and unsaturated hydrocarbon fractions. Clearly separated fractions can be seen in the chromatogram (Figure 1) accompanying this separation process.

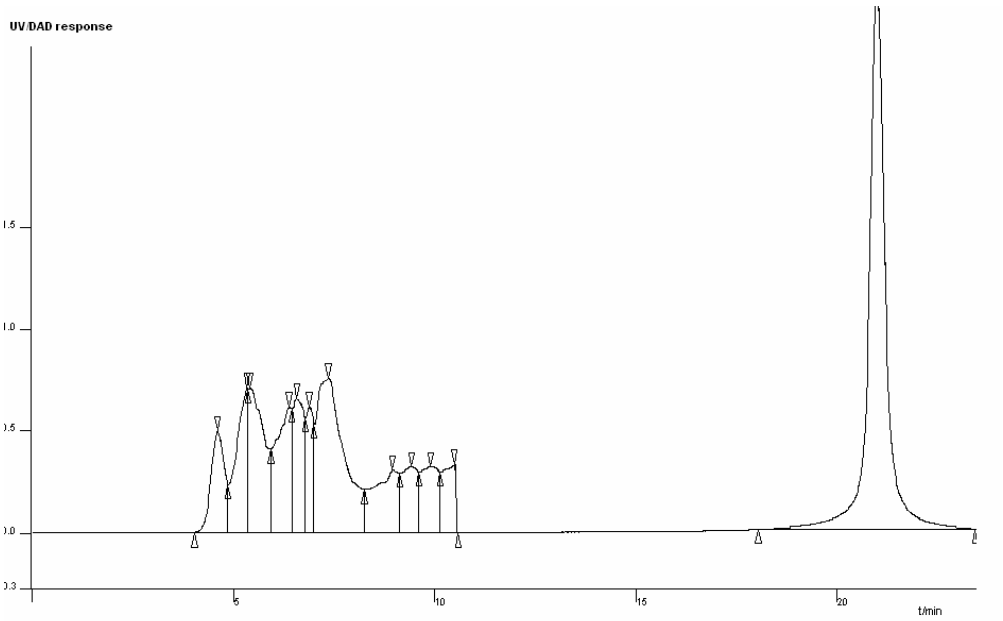

Figure 2: NP-HPLC chromatograms of gas oil

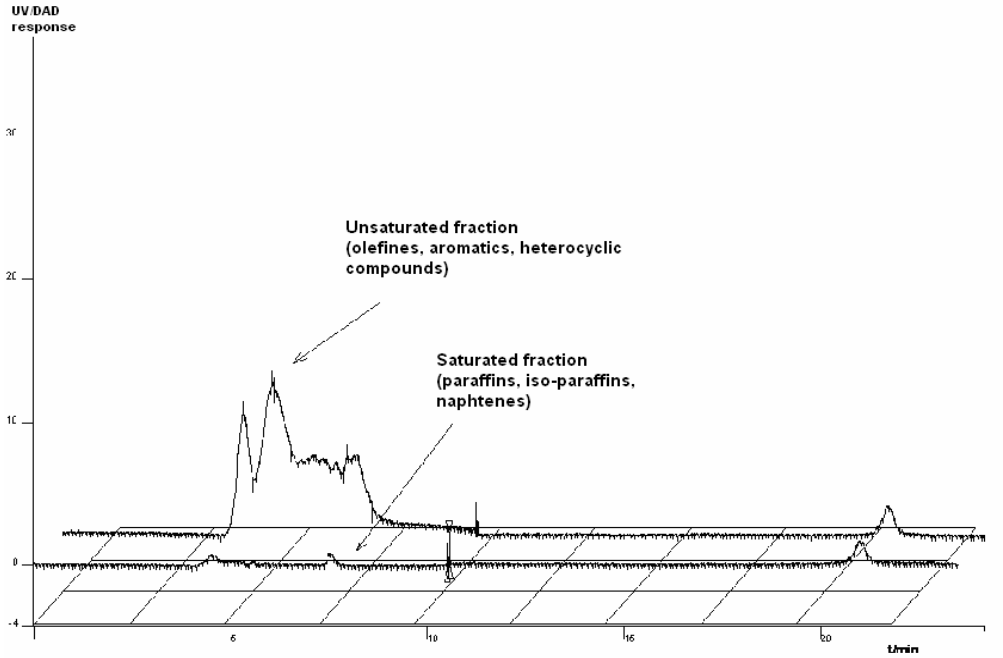

Figure 3: NP HPLC chromatograms of saturated and unsaturated fractions of gas oil

The NP HPLC method was used to analyse the entire gas oil which has not been subjected to the separation and its chromatogram (Figure 2) shows a complex hydrocarbon mixture. Saturated and unsaturated hydrocarbon fractions were chomatographically analysed and the group compositions of both fractions were qualitatively determined (Figure 3).

The comparison of the chromatograms shows that unsaturated particles are present in the saturated fraction in trace amounts. This confirms that the level of separating saturated from unsaturated hydrocarbon groups on silver-modified column was very high. The presence of olefine hydrocarbons in the unsaturated fraction was confirmed by comparing the chromatogram of the unsaturated fraction to the chromatogram of the olefine standard (Figure 4). Thus this analytical approach solves the problem of the coeluation of saturated and unsaturated fractions in the NP HPLC analyses on an amino-modified silica gel column.

The problem of the shown fractionation method is that due to the dimensions of a silver modified column (analytical column, a filler particle size is 10 μm) only the fractionation of a small initial quantity of gas oil samples is possible, and the fractionation was repeated for several times in order to retain a sufficient quantity of certain fractions needed for the further analysis after removing a solvent. This

significantly complicates the possibility of the quantification of certain hydrocarbon groups which would also be desirable. We also intend to work on a preparatory chromatography column of larger filler particles which would provide a bigger initial quantity of the analysed sample. Apart from the NP HPLC method the separated hydrocarbon fractions can also be analysed by the use of other analytical techniques (for example, GC, GCxMS, GCxGC, NMR and the like), which usually make quality and quantity analyses more complicated due to the complex composition.

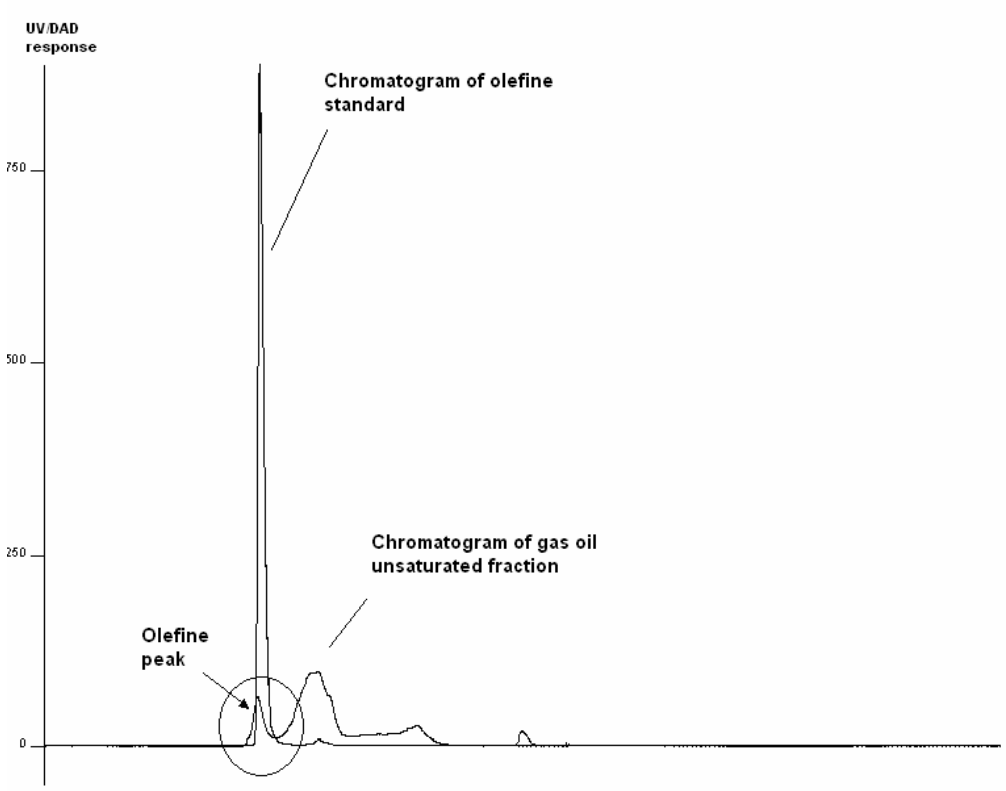

Figure 4: NP HPLC chromatograms of olefine standard and unsaturated fractions of gas oil fraction.

Conclusion

The paper shows the two step liquid chromatographic analysis of gas oil. In the prefractionation step, on the silver-modified silica gel column, saturated hydrocarbon fraction was separated from the unsaturated one. The fraction purity was confirmed by the further NP HPLC analysis. In the NP HPLC chromatogram of the saturated fraction there are unsaturated particles in trace amounts. The presence of olefine

hydrocarbons in the unsaturated fraction was confirmed by comparing the chromatogram of the unsaturated fraction of gas oil to the olefine standard. Further work on the quantification of separated groups is required in order to get a more complete insight into the hydrocarbon composition of gas oil.

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