NAPHTHA POOL OF COMMERCIAL GASOLINE AND NIR-SPECTRUM PATTERN

A. Andziulis

Klaipėda University

1. Introduction

Modern commercial high-octane gasoline (research octane number $RON \geq 92 \div 98$ and motor octane number $MON \geq 82$) is obtained by blending over N_{napht} >10 various oil and its heavy residuum refining technologies naphtha (reformate, FCC etc., Fig 1) with ethers or spirits (oxygenates, $N_{oxg} > 6$) and their mixtures. According to this there can be under $N_{hydroc} < 500$ hydrocarbons with different octane numbers (*ON*) and other important characteristics for gasoline (LST EN 228) in naphtha solution. Basically they are C5 – C8 hydrocarbons with C4 and C9 – C10 admixtures.

Today oil refinery plants of older construction (LK6Y + KT1/1) have only low knock stability light straight run (LSR) and heavy fraction part (SR, $ON \approx 60$). The high-octane has only: reformate (Ref., $RON \approx 96$) with very plentiful aromatic ($K_{arom} > 60$ %), fluid catalytic cracking naphtha (FCC, $RON \approx 92$) with too big olefin amount ($K_{olef} \approx 20$ %) and methyl tert-butyl ether – MTBE, $RON_{MTBE} \approx 112 - 130$) octane number of which usually depends on purity and other small gasoline technologies (thermal cracking – TC, olygomerisation – Olyg.) the products of which according to new environmental requirements have problems of quality. That is why, while choosing some

kind of methodology, it is important to discuss what naphtha pool of gasoline technologies is purposeful to modernize or to become familiar with seeking not only to increase ON, but also to estimate toxic emission of their combustion products [2, 3].

2. Purpose, object and method of research

The purpose of this work is according to IR – spectrum research also chromatography, physical and knock stability research, of different naphtha (straight run, reforming, catalytic cracking, olygomerisation, thermal cracking and MTBE), to prove some structure of "hypothetical (effective) molecule" of commercial gasoline mixture meeting new environmental requirements and saying that a separate component, appropriate to gasoline quality can only partially supplement a field of fractional composition.

Research object is a set of fragments in predominating hydrocarbons (structure-functional =CH, =CH$_2$ and –CH$_3$ groups in different paraffin, naphthenes and aromatic skeletons) of different technologies naphtha (Ref., FCC and other) as totality [Fig 2].

Research method is based on intensities of IR-spectrum pattern lines which are sufficiently well associated with octane number of gasoline and it also shows gasoline ability to burn [4–6].

Research and experiment methods:

– the optical characteristics of samples in medium and near IR-spectrum patterns have been studied with special IR-spectrometers [5]. In medium IR-pattern ($\lambda = 6 - 14$ μm), with some kind of problems, valence vibrations of structure groups of molecules and vibrations of deformation intensities of plain molecules skeletons were observed. In near NIR- spectrum pattern ($\lambda = 0,7 - 1,7$ μm; $\Delta\lambda = 2$ nm; $T_{NIR} = 300$ K) their overtone-3 appears and integrates well. We want to emphasize, that the variation $d_{cell} = 0,5 - 10$ cm of
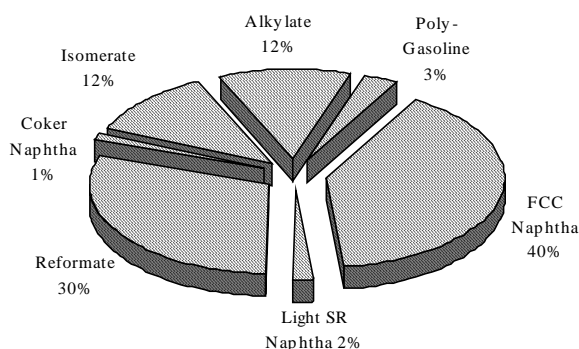

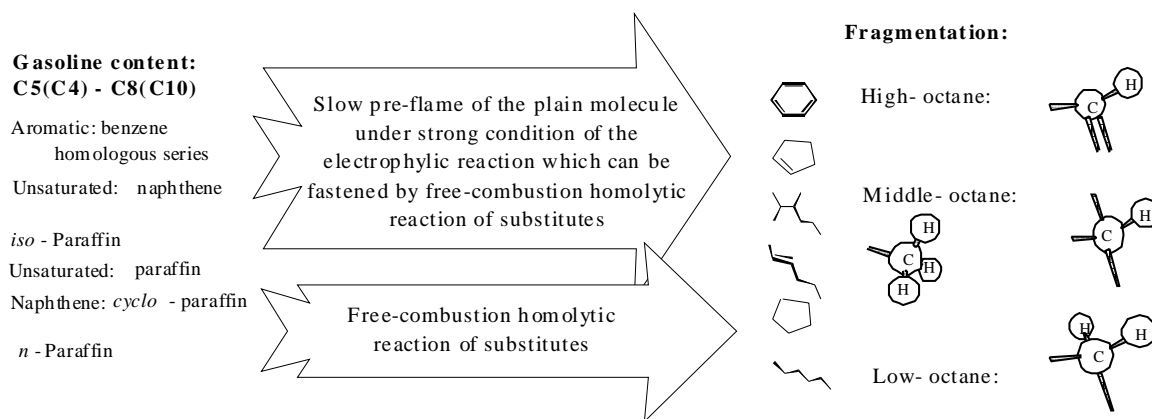**Fig 1** . Typical gasoline pool composition in the USA [1]

Fig 2. The association of gasoline octane number with the set of fragments of hydrocarbon molecules

optical cell thickness is obligatory, because the input of benzene and its homologues into gasoline *ON* is essential ($ON_{arom} > 100$), but their coefficients of overtone-3 absorption in NIR-pattern are small, comparing with the absorption coefficients of paraffin and naphthenes overtone-3;

– hydrocarbon content of naphtha samples was determined by CARLOSERBA chromatograph. The information about amounts of benzene (K_{ben}) and toluene (K_{tol}) was made more accurate with the help of Autosystem XL Gas Chromatograph (EN 12177:1198);

– the characteristic of distillation was studied according to ASTM D86;

– octane numbers *RON* and *MON* were tested by standard engine procedures (ASTM D2699 and ASTM D2700) and compared with results of ZX 101C octane NIR-tester (Zeltex Inc., $\lambda = 0,8 - 1,2$ µm).

3. Materials and results

3.1. The conception of gasoline blending

Not long ago in Europe (The ACEA Fuel Charter, 1994) and USA (SAE) construction of Otto engine was optimised choosing commercial gasoline with conceptually different content of hydrocarbons which is obtained by blending various naphtha.

Europe in its conceptions turned to gasoline with very high-octane. This gasoline is used for economic lower cubic capacity, but higher compression coefficient engines. According to this the octane number of "modern" fuel sorts was ideal, when $RON \geq 95 \div 98$ and motor $MON = 85 - 89$ (e.g. "Aral" gasoline, 1993). That praised reforming (platforming) technology in Europe oil refinery (e.g. JSC "Mazeikių nafta" $K_{Ref} \approx$

80% v/v). This technology transforms (dehydrocyclization) low-octane n-paraffin ($ON_{C6-C8} \leq$ (-20 – +20)) into aromatic ($ON_{C6-C8} = (99 - 113)$). When conversion level is over $K_{paraf?arom} \geq 60$ % reformate naphtha $RON_{Ref} \geq 96$. The amount of blended reformate in gasoline naphtha pool is limited because the ignition of benzene ring starts slowly and under strict conditions according to oxidation S_E-mechanism (Fig 3) (without "cold pre-flame phase") and only then goes into fast combustion S_H-mechanism, therefore aromatics combusts not entirely and pollutes environment very much.

But nowadays when "the Clean Air Act" became a priority it does not seem that USA (SAE) has gone to better direction choosing lower compression, but bigger cubic capacity engine constructions and creating "ecologically clean fuel" ($K_{arom} \leq 27\%$ v/v) the *ON* of which is being increased by big amount of oxygenates MTBE ($K_{oxg} \approx 11 - 18\%$ v/v). The low-octane index $OI = 1/2 \cdot (RON + MON) \geq 88$ of this is determined by prevailing iso-paraffin in it. That is because of diminishing the amount of reformate in the pool of reformulated gasoline approximately twice and increasing the content of FCC naphtha, alkylate and isomerate
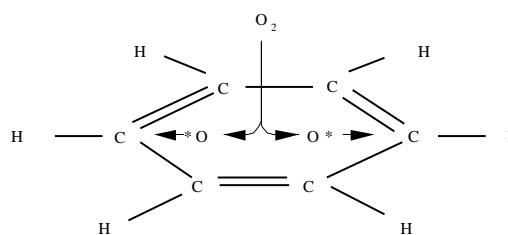

Fig 3. Pre-flaming of benzene and not benzene plain systems (cycle-olefins etc.) according to electrophilic reaction (S_E)

(Fig 1). Pay attention that MTBE which $RON_{MTBE} \approx 112 - 136$ is a well burning product. Thereby it was quite motivated for refinery plants to build MTBE unit. But namely this big MTBE usage surprisingly caused a new ecological problem – the pollution of ground water. Tests showed that water pollution emerged in USA states (California, Maine etc.), that mostly use reformulated gasoline. MTBE is sufficiently dissolving, stable, water polluting and it gets into the ground with gasoline in its storing and overflowing terminals. Therefore oil refinery companies have already prepared projects to revamp MTBE units into production of iso-octane (Nexoctane technology) or etherisation gasoline [7–8].

Thus, the question is how to produce gasoline with high *ON* (e.g. *Unleaded Petrol "Super" grade* 98) in accordance with today's index of quality (LST EN 228), if hydrocarbon groups with remarkably high-octane (aromatic, olefin and MTBE) recently are unwanted in it. There are some problems to replace those groups with other high-octane hydrocarbons, because it is hard to produce fully izomerizated paraffins ($ON \cong 100$) in alcylation and isomerisation processes even using molecule filter (e.g. Penex + Molex technol.).

In this work knock stability conception is based on a photochemical effect, stimulated by pre-flame mechanism, saying that not clear (according to ON) Fuzzi set of hydrocarbons (paraffins, naphthenes, olefins, aromatic and oxygenates), during burning process emits excitation energy ($E*$) of intermolecular interactions of deformation vibrations by quantum ($h\nu$). This quantum helps to crack oscillation system – hydrocarbon molecule into fragments with different *ON* (Fig 2). These fragments integrate in a new set and make vision of "hypothetical molecule" in combustion cavity. That is motivated observing the set of definite gasoline naphtha pool oscillation IR-spectrum lines intensively, straight ($\Delta ON \leq 0,7 \div 4\%$) regression with fuel technical parameters – octane numbers *RON* and *MON* in this and other works:

$$ON(RON;\ MON)_{i,j} = \bar{y}_{i,j} + \sum_{i=1}^{k=m} q_{i,j,k} \cdot x_{i,k}, \qquad (1)$$

here: i is number of samples; j - is version of technology; k shows what is calculated *RON* or *MON*; m – the number of controlled points in NIR-spectrum; $\bar{y}_{i,j}$ - specific deviation for concrete naphtha, precision of

which depends upon the number of calibration tests ($p* = 30 - 300$) [9].

Besides that, for the swift work of engine (2) not only octane number is important, but also characteristics of fuel distillation [10]:

$$DI = 1,5\ T(10) + 3,0\ T(50) + 1,0\ T(90), \qquad (2)$$

here: $T(10, 50, 90)$ – points of distillation characteristics.

This characteristic, in accordance with (LST ISO 3405, ASTM D 86), includes these distillation points: $T_{D1} = 70°C$ (E 70); $T_{D2} = 100°C$ (E 100); $T_{D3} = 180°C$ (E 180) and $T_{FBP} \leq 215°C$. Besides that, vapour pressure characteristic which limits the content of low boiling isomers in gasoline up to $10 \div 40\%$ v/v., is important too.

That is why reformate with FCC naphtha of a wide $T(0 \div 100)$ fractional content has to prevail in modern commercial recipes of gasoline (Fig 4). Then alcylate, isomerate and nexoctane can be mixed in. We can mix the second-quality oligomerate TC and other small naphtha into second-grade sorts of gasoline.

3.2. Discussion of results

In typical chromatograms of gasoline naphtha pool there are much more (peaks) lines ($N_{hyc.} \leq 150$), than hydrocarbons ($N_{hyc.} \leq 40 \div 60$) with known knock stability (RON_i and MON_i). That is why even the use of precise chromatographs counting gasoline knock stability does not give good results (1) without using the method of molecule defragmentation ($\Delta ON \approx 2 \div 5\%$) [11]. Thus, it is identical to fast IR-method.
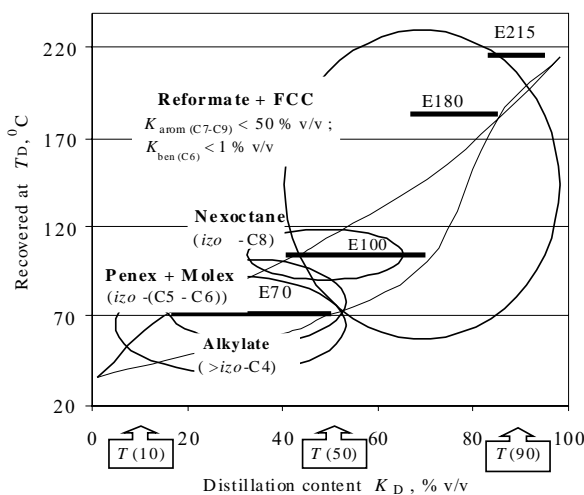

Fig 4. Optimal fractional content of swift gasoline ($RON \cong 95$ - 98 and the technological variant of its realization
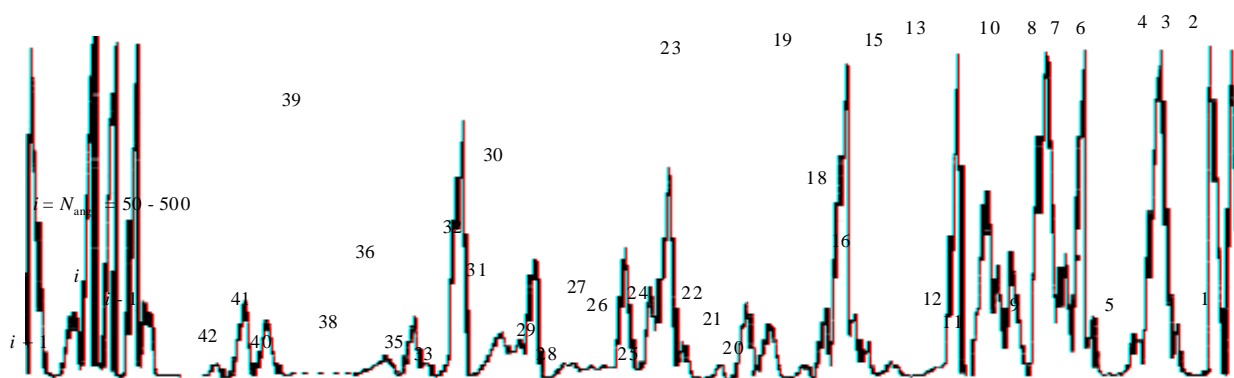
Fig 5. A typical chromatogram of FCC naphtha where up to 150 lines are being observed

For typical naphtha pool (SR, Ref., FCC, TC) and solution of gasoline the vibration line-shift from fundamental tone in medium IR-spectrum pattern by various content of hydrocarbons in the specimens

Content / Wavelenght	Hydrocarbonaceous composition / medium IR-wavelength / line-shift from fundamental tone					Substitute: -CH$_3$		$\equiv$C-H
	Aromatic (ring, $\equiv$CH)	Naphthene (ring, =CH$_2$)	n-, iso-Paraffin (=CH$_2$)	Unsaturated (C=C)	Unidentified	Sym. vibration	Asym. vibration	Deformation vibration
K_i, % wt.	8,29÷53,38	4,5÷39,73	32,31÷51,55	0,23÷31,61	0,04÷1,98			
λ_i, μm	6,22 ÷ 6,23	9,66 ÷ 9,71	13,33 ÷ 13,79	6,04 ÷ 6,12		7,25	6,85	10,26÷10,42
Naphtha $\leq \Delta\lambda_{i,j}$, nm	10	47	459	80		0	0	160
Solutions $\leq \Delta\lambda_{i,j}$, nm	40	94	272	25		79,6	160,1	111

*experimental data in the range investigations of higher significance [11, 12]

The research results of IR-spectrum of typical vibration of structure groups (=CH$_2$, $\equiv$CH, Fig 2) and substitutes (-CH$_3$, =CH$_2$CH$_3$) of hydrocarbon molecules in different skeletons (paraffin chain, benzene or naphthene ring) are summarized in Table. We should mark that in different gasoline wave lengths (λ_i) of typical vibration of structure groups differently changes in time ($max\Delta\lambda_i(t) \approx 0 ÷ 459$ nm) and depends on hydrocarbon composition of gasoline, technological factors etc. Particularly it is complicated and not predictable when mixing different naphtha. Therefore, counting octane number of gaso-

line blending, according to IR-tests, when parameters $p < p^*$, we should pay attention, that the arguments of equation are time functions $\bar{y}_{i,j}(t)$ and $q_{i,j,k}(t)$ with some kind of precession in time which is not discussed in theory yet. It can be explained as not fully revealed problem of formation of the ratio of real, limited solution and azeotropic compositions in the general complex of big hydrocarbon systems ($140 \leq N_{hyc.} \leq 500$).

The observed deviation of typical vibration lines ($\Delta\lambda_i(t)$) in NIR-spectrum (Table) are characteristic to their overtones too. In Fig 6 we can see that the inten-
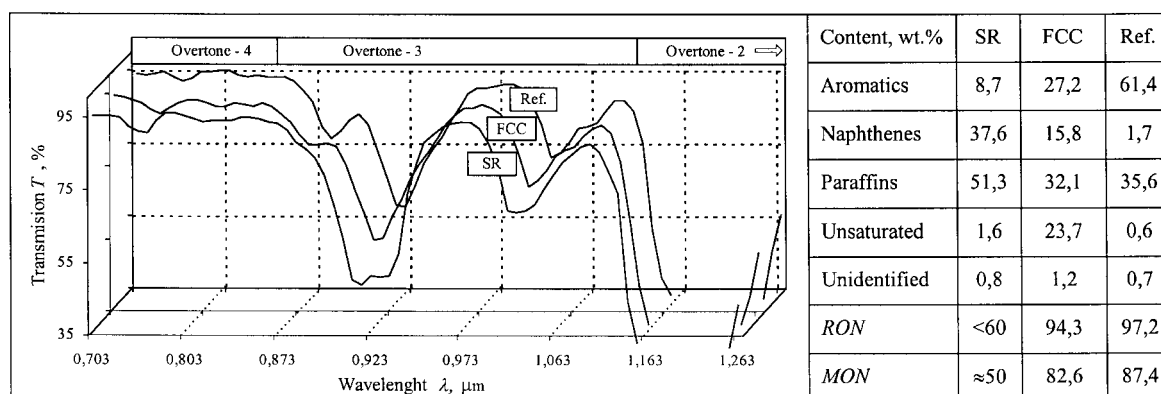

Content, wt.%	SR	FCC	Ref.
Aromatics	8,7	27,2	61,4
Naphthenes	37,6	15,8	1,7
Paraffins	51,3	32,1	35,6
Unsaturated	1,6	23,7	0,6
Unidentified	0,8	1,2	0,7
RON	<60	94,3	97,2
MON	≈50	82,6	87,4

Fig 6. NIR-spectrum pattern of naphtha (straight run – SR, FCC naphtha, reformate – Ref.) in overtone-3 range and its content
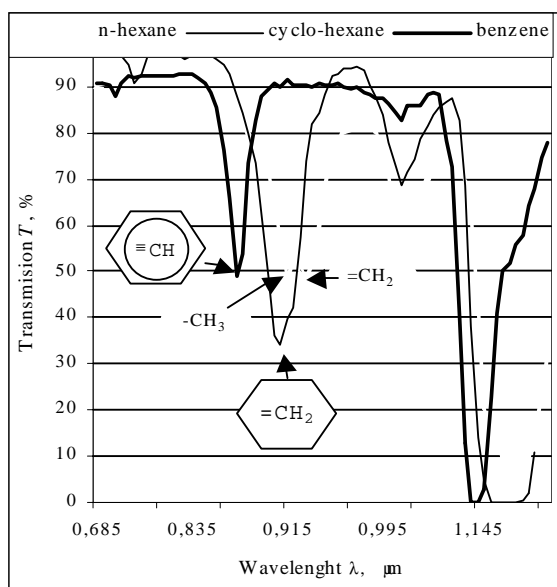
Fig 7. Hydrocarbon reforming and NIR-spectrum pattern

Fig 8. Skeleton isomerism and NIR-spectrum pattern

sities of overtones have the following sequence $T_{overt-4} \ll T_{overt-3} \ll T_{overt-2}$ and $T^3_{ben} \ll T^3_{napht} \approx T^3_{CH_2} \approx T^3_{CH_3}$. Because strong overtone-4 lines interflow with other IR-spectrum lines, and overtone-2 lines are very week modern NIR-testers of octane numbers (PIONIR 1024, Zeltex-101C, Zeltex-440) operate with absorption intensities of overtone-3 ($\lambda_i = 0{,}7 \div 1{,}2$ mm). Practical use of these NIR-testers in technologies is decreased not only by the calculated overlap of interflowing lines, but also by their not predictable distorting due to the shift ($\Delta\lambda_i(t)$) and because of a contrary functioning of substitutes –CH₃ and –CH₂CH₃ in different fragments, as we shall discuss later. In Fig 7 and Fig 8 we can see that absorption of individual hydrocarbons in NIR-spectrum is clearly expressed by lines of molecule fragments overtone-3: $\lambda^3_{CH_2} \cong 929{,}8$ nm - low octane =CH₂ in paraffin skeleton, $\lambda^3_{naph} \approx 922$ nm - ring of not high-octane naphthene (=CH2)*, $\lambda^3_{ben} \cong 871$ nm - especially high-octane benzene ring (≡CH)*, and $\lambda^3_{CH_3} \cong 915{,}9$ nm - line of substitute in high-octane paraffin skeleton –CH₃.

It is easy to observe alcylation and isomerisation processes by NIR-method where n-paraffins and n-olefins transform into iso-paraffins. It is particularly relevant to isomerisation technologies of several levels with molecular filters where efforts are being made to maximize the isomerisation of product. In this case (Fig 8), in NIR-spectrum, a line $\lambda^3_{CH_2}$ disappears and $\lambda^3_{CH_3}$ line becomes well defining and reflects high-oc-
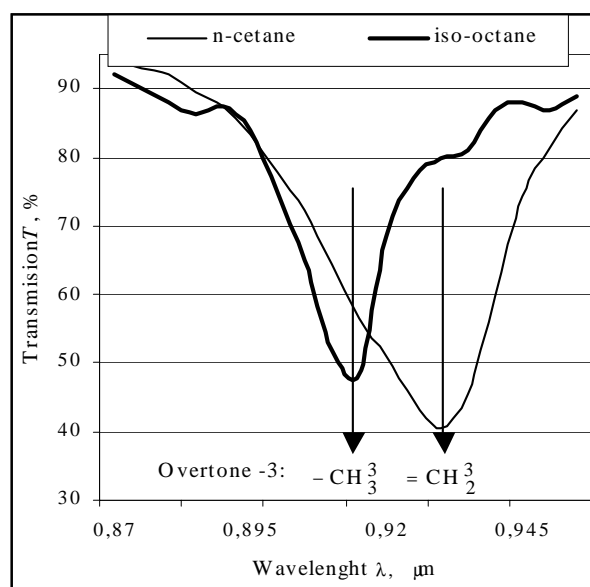
tane number (ΔON (n =1) ≤+21,2). It is more complicated with reforming and FCC naphtha. A raw material of reforming technology – SR naphtha has NIR-spectrum of all fragments: the faint line λ^3_{ben} which reflects low aromatic concentration interflowed and overlapped $\lambda^3_{CH_2}$, λ^3_{naph}, $\lambda^3_{CH_3}$ lines. Reformulating (Fig 6, Fig 7) n-paraffins and naphthenes into aromatic, in IR-spectrum the lines associated with high–octane λ^3_{ben}, $\lambda^3_{CH_3}$ become clearly expressed and the ones with low-octane λ^3_{naph} are disappearing. The problem is that, by eliminating benzene from reformate and FCC, the role of plain molecules in gasoline remarkably increases. The appearance of substitutes –CH₃, -CH₂CH₃ and the increase of their number are connected with the change of oxidation reaction of molecules, that is the pre-flame of a plain molecule (benzene ring) starts with the fast homolytical reaction of a substitute. It is associated only with the decrease of ON: for aromatic - $\Delta ON = 0 \div -10$, for paraffin – ΔON =-6 ÷ –23; and it naturally causes a shift of lines (1) in the deformation vibration of an oscillator. Thereby when paraffin, naphthenes and aromatic exist together in naphtha solution, an indeterminate occurs in valuing the intensity of line (1) $\lambda^3_{CH_3}$, because there is a constituent with both positive and negative sign.

4. Conclusions

1. Nowadays according to new environmental research two main hydrocarbon groups (aromatic, ole-

fins) and MTBE of very high knock stability (*ON*) are unwanted in gasoline. The only isoparaffins have not been criticized yet, which give products with *ON* <100 in existing isomerisation and alcylation technologies. Therefore it is necessary to consider an optimum ratio of new gasoline technologies choosing some kind of methodology. An important fuel distillation characteristic can be realized in modern technology by mixing alcylate, isomerate, FCC, reformate (accentuated in higher benzene homologous) and then other naphtha, watching that iso-skeleton and rings of benzene with -CH$_3$ substitutes in gasoline structure should prevail.

2. The application of IR-rays methodology is sufficiently accurate when researching or testing the gasoline knock stability (*ON* ≤ 0,7 ÷ 4 %) of different naphtha pool of various technologies; especially allotting lines of overtone-3 $\lambda^3_{CH_2}$, λ^3_{naph}, λ^3_{ben} and $\lambda^3_{CH_3}$, or evaluating the part of not burning benzene rings in the set of "defragmented" hydrocarbons in engine capacity.

3. Seeking for a wider use of NIR-method for testing naphtha solutions it is necessary to solve the problem of identification of formation of real, limited solution or azeotropic compositions in the general complex of big hydrocarbon systems (140 ≤ $N_{hyc.}$ ≤ 500) by the line-shift in NIR-spectrum pattern.

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PREKINIO BENZINO KOMPONENTŲ FONDAS IR ARTIMA *IR*-SPINDULIUOTĖ

A. Andziulis

Santrauka

Šiandien naftos perdirbamojoje pramonėje iškilo problema, kaip gaminti didelio detonacinio atsparumo (*RON* ≥ 95 ÷ 98, LST EN 228) neetilintą benziną, kai pagal naujus aplinkosauginius tyrimus dvi pagrindinės ypač didelio detonacinio atsparumo (*ON*) angliavandenilinių grupės (aromatika, olefinai) bei oksigenatas MTBE benzine yra nepageidaujami. Nekritikuoti liko keli didelį oktaninį skaičių turintys izoparafinai, kurie sukuria didelio lakumo produktus su *ON* mažesniais negu 100. Todėl, pasirinkus tam tikrą metodologiją, pvz., NIR-spektroskopijos metodą, būtina iš naujo aptarti naujų technologijų santykį benzino gamyboje.

Šiame tyrime parodoma, kad daugeliu atvejų IR-spinduliuotės metodologijos taikymas yra pakankamai tikslus tiriant ar testuojant įvairių technologijų benzino komponentų (*naphtha*) detonacinį atsparumą (*ON* ≤ 0,7 ÷ 4 %), ar vertinant degančių angliavandenilių aibėje toksinių benzeno žiedų dalį bendroje „defragmentuotoje" (≡CH, =CH$_2$, ir –CH$_3$ struktūrinės grupės parafinų, naftenų ir aromatikos karkasuose) aibėje.

ARŪNAS ANDZIULIS

Doctor, Associate Professor, Department of Technological Processes, Klaipėda University (KU), Bijūnų g. 17, LT-5802 Klaipėda, Lithuania. E-mail: aandz@ip.ku.lt

Doctor of Science. First degree in Materials Science, 1985, Kaunas Technology University (KTU). Publications: Author of ≥ 60 scientific publications, 2 inventions and 12 research and development designs. Research interests: oil processing and petrochemistry, the infrared spectra of complex molecules, automotive emissions etc.