

Separation and Characterization of Polycyclic Hydrocarbons from Georgian Petroleum

Giorgi ARESHIDZE¹, **Khatuna BARBAKADZE**¹, **Witold BROSTOW**², **Tea DATASHVILI**², **Osman GENCEL**^{2,3}, **Nodar LEKISHVILI**^{1*}, **Erna LEKVEISHVILI**^{1,4}

¹ Department of Chemistry, Ivane Javahishvili University, 1 Ilia Chavchavadze Avenue, 0128 Tbilisi, Georgia

² Laboratory of Advanced Polymers & Optimized Materials (LAPOM), Department of Materials Science and Engineering and Center for Advanced Research and Technology (CART), University of North Texas, 1150 Union Circle # 305310, Denton, TX 76203-5017, USA; <http://www.unt.edu/LAPOM/>

³ Department of Civil Engineering, Faculty of Engineering, Bartin University, Bartin, Turkey

⁴ Petre Melikishvili Institute of Physical and Organic Chemistry, 5 Jikia Street, 0186 Tbilisi, Georgia

Received 29 December 2009; accepted 18 March 2010

A novel method of isolation of polycyclic aromatic hydrocarbons (PAHs) from three Georgian petroleum fields has been developed. PAHs are classified as carcinogenic compounds and monitored worldwide in a wide range of environments including drinking water, waste water, furnace emissions, soil, hazardous waste extracts and in air over major cities. Our method is a combination of photo-chemical condensation of petroleum PAHs via reaction with maleic anhydride, followed by photodecomposition of resulting photo-adducts. Extraction with gas-liquid chromatography constitutes a final step for isolating narrow fractions of phenanthrene, naphthalene and benzene. Gas-liquid chromatography, mass spectrometry, chromato-mass spectrometry and spectrofluorimetry were used to analyze individual compounds. Our method of isolation of PAHs can be successfully used for crude petroleum, petroleum fractions and for petroleum-derived materials – in spite of differences in their compositions.

Keywords: petroleum characterization, polycyclic aromatic hydrocarbons, maleic anhydride, separation, photo-adducts, petroleum products.

1. INTRODUCTION

Effective use of petroleum is based on characterization of the crude oil and then after separation into fractions of appropriate characterization of the fractions [1–12]. As pointed out by Jaramillo and her colleagues [13, 14], the use of petroleum is on the increase – with severe consequences for CO₂ emissions and for economies of entire countries. Jaramillo, Griffin and Matthews show that using gas-to-liquid fuels involves problems also. Further, as noted by Pyshev and his colleagues [10], straight-run petroleum fractions usually do not meet requirements for products such as gasoline or Diesel fuel. As discussed by Lucas and her colleagues [9], petroleum contains a variety of organic compounds, including polycyclic aromatic hydrocarbons (PAHs). PAHs are a large group of compounds with two or more fused aromatic rings. They either occur naturally in fossil fuels – coal and petroleum – or are released from combustion of fossil fuels and degradation of manufactured materials such as lubricating oils, dyes, detergents and plastics. Terrestrial PAHs are predominantly formed via pyrolysis, dehydrogenation and incomplete combustion of biogenic material [15]. PAHs have been found throughout the universe, specifically in carbonaceous chondrite meteorites, Martian meteorites and interplanetary dust particles.

PAHs are classified as carcinogenic compounds, consequently they are monitored worldwide in a wide range of environments including drinking water, waste

water, furnace emissions, soil, hazardous waste extracts and in air over major cities [16, 17]. They have a relatively low solubility in water but are highly lipophilic (soluble in fats, oils, lipids, and non-polar solvents such as hexane or toluene). Most PAHs are toxic while carcinogenic are mainly those with four or more rings [18]. The wide distribution of PAHs in the environment poses serious health risks to all living organisms. High concentrations of PAHs in sewage effluents and urban runoffs are due to contamination from petroleum and petroleum products, mainly from lubricating oils. In the absence of proper treatment and disposal procedures, lubricating oils after use cause a serious threat to our environment.

In this situation, a simple, fast, precise and efficient method to isolate, identify and measure the levels of PAHs in our environment is necessary both for the regulatory control of disposal of used lubricating oils and for risk assessment of PAHs to living organisms. Liquid-liquid extraction (LLE) has been applied to PAHs in lubricating oils. However, LLE method consumes much time and requires large amounts of organic solvents – that cause a different kind of pollution. We describe below an alternative method that does not suffer from drawbacks of LLE.

2. EXPERIMENTAL PART

2.1. Materials

Various methods have been used to study petroleum from Noryo, Mirzaani and Samgori fields in Georgia for a long time [19, 20]. Properties of petroleum samples studied by us are listed in Table 1.

* Corresponding author. Tel.: +995-32-294794; fax: +995-32-001153.
E-mail address: nodar@lekishvili.info (N. Lekishvili)

Table 1. Properties of petroleum from Noroyo, Mirzaani and Samgori fields

Field	Type	Density, d_4^{20}/gcm^{-3}	Engler viscosity, η_{50}	Content of resin, wt. %	Solid paraffin, wt. %	Sulfur, wt. %
Noroyo	naphthenoaromatic	0.89	1.55	32	0.80	0.15–0.23
Mirzaani	naphthenic	0.86	1.60–1.65	30–34	0.82	0.22–0.25
Samgori	naphthenoparaffinic	0.84	2.6	7.0	14.7	0.17

Reagents were supplied by Sigma Chemicals Co. They were analytical grade and were used as received.

2.2. Gas chromatography (GC) and mass spectrometry (MS)

We have used a LHM-80 gas chromatograph (Moscow, Russia) with a flame ionization detector. The chromatographic column was 3.0 m in length with an inner diameter of 4.0 mm. Chromatographic packing was 5 wt. % SE-30 on Chromosorb W; helium used as a gas-carrier. We have used Finnigan 4021 and LKB-2091 (Bromma, Sweden) mass spectrometers.

2.3. Luminescence Analysis

We have used luminescence spectroscopy to analyze aromatic compounds. The tests were conducted at 25 °C and –176 °C. During the analysis in frozen state three types of irradiation sources have been used, namely fluorescence, phosphorescence and excitation luminescence [21].

We have used a Baird Atomic (Cambridge, MA) Fluoricord to record fluorescence spectra. Absorption spectra at room temperature were recorded in the 200 nm–350 nm range, using a Carl-Zeiss USU-2-P spectrophotometer (Jena, Germany).

2.4. Synthesis of Photoadducts

The process was carried out in a reaction flask equipped with a condenser at 10 °C–15 °C with constant stirring under nitrogen atmosphere in n-hexane solution. Photoadducts were synthesized via a photochemical reaction between a petroleum fraction (2.5 g) and maleic anhydride (10.0 g) in the presence of benzophenone (2.5 g). The resulting mixture was then subjected to 10 wt. % KOH solution. Photoadducts were obtained after neutralizing the system with acid and evaporating the solvent from the mixture. The yield was 50 wt. %–60 wt. % for Noroyo field petroleum, 30 %–40 % for Mirzaani petroleum and 20 %–30 % for Samgori petroleum.

2.5. Photodegradation of Photoadducts

We have performed irradiation of the adducts in ethanol solution. Typically, at first 1 g of adducts was dissolved in 300 ml ethanol and the resulting mixture irradiated with a mercury-quartz lamp under nitrogen atmosphere for 15 hrs at 10 °C–15 °C temperature. After evaporation of the solvent, warm (50 °C–55 °C) KOH solution was applied.

Afterwards n-hexane, benzene and distilled water were used to extract and wash isolated PAH concentrates. Final products were dried at 35 °C–40 °C under vacuum. The yield of PAH from the adduct was 58 wt. %–65 wt. %.

2.6. Separation of narrow AH fractions

Gas-liquid chromatography was used to separate narrow PAH fractions from photodegradation products. 2.15 g PAH concentrate was dissolved in 10 ml solvent; n-hexane and benzene were used as solvents. The chromatographic column was 0.5 m in length with an inner diameter of 1.5 cm, filled with 30 g Al_2O_3 . Before each test, sorbent activation was achieved by maintaining at 400 °C for 4 hrs. Elution was performed at room temperature using n-hexane and benzene; extraction was performed using hot (65 °C–70 °C) benzene and dioxane (25 °C).

The following six eluates were obtained: n-hexane and benzene (#1, 2), extracts of benzene from upper and lower zone of adsorbent in the chromatographic column (#3, 4) and dioxane extracts from upper and lower zone of the adsorbent (#5, 6).

3. ISOLATION AND SEPARATION OF HIGH-BOILING AROMATIC HYDROCARBONS

A stepwise method developed to isolate aromatic hydrocarbons (AHs) from petroleum and petroleum products is described above in Section 2.4–2.6.

We have found that variation of conditions of the photo-condensation process affects the products obtained. Higher concentration of naphthalene hydrocarbons were formed for lower (1–2 hrs) irradiation times. Longer times up to 6 hours lead to formation of phenanthrenes. Further irradiation (7–28 hrs) causes predominant formation of benzene hydrocarbons.

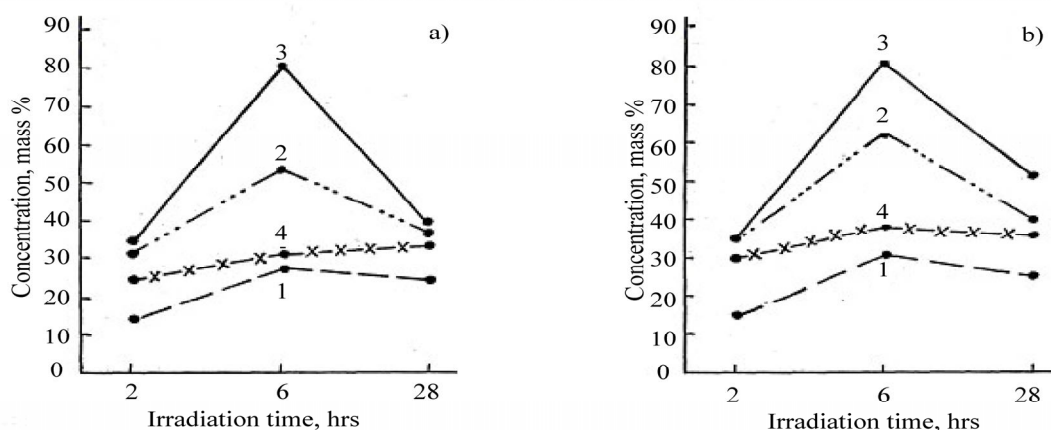
Narrow aromatic concentrates isolated from Noroyo, Mirzaani and Samgori petroleum fields were analyzed by gas chromatography (GC) and mass-spectrometry (MS). They were extracted from Noroyo oil at 498 °C–510 °C (Sample 1), Mirzaani oil at 490 °C–505 °C (Sample 2) and Samgori oil at 450 °C–500 °C (Sample 3) fractions at 6 hrs illumination. Table 2 shows AHs content in the benzene concentrates.

Despite differences in composition of the initial petroleum from various fields, we seen in Table 2 that concentrations of phenanthrene hydrocarbons including alkyl- and naphtho-phenanthrenes in Samples 1 and 2 are approximately the same while that concentration is lower in Sample 3.

Influence of other factors such as solvents nature and the temperature on the effectiveness of the photocondensation process and subsequently on the yield of extracted materials was also examined. Figure 1 shows the respective results for the Mirzaani field 460 °C–475 °C petroleum fraction. Since each curve consists of only three points, locations of the maxima are necessarily

Table 2. Benzene extracts (explanation in text)

№	Type of the compound	Degree of unsaturation	Sample		
			1	2	3
1	Alkylbenzenes	6	3.5	3.0	5.3
2	Indenes (Tetralins)	8	–	–	1.2
3	Dinaphtenobenzenes	10	3.7	4.3	6.7
4	Naphthalene	12	3.7	2.5	6.7
5	Acenaphtene	14	–	4.1	5.9
6	Fluorene	16	–	3.8	3.0
7	Phenanthrenes	18	59.7	71.2	63.2
8	Naphtenophenanthrenes	20	22.1	9.8	6.3
9	Pyrenes	22	3.6	1.3	1.7
10	Chrysenes	24	3.7	–	–
11	Phenanthrenes + naphtenophenanthrenes		81.8	79.9	70.1
12	Alkylphenanthrenes + naphtenophenanthrenes + pyrenes + chrysenes		89.1	80.0	71.2

**Fig. 1.** Influence of the irradiation time and solvent nature on the extraction of alkyl- and naphtenophenanthrenes (a) and phenanthrenes and their benzene analogues (b) concentrates from the Mirzaani field 460 °C–475 °C petroleum fraction. 1 – n-hexane; 2 – benzene; 3 – hot (70 °C) benzene; 4 – 1,4-dioxane

approximate. On the left side (a) we show results for extraction of alkyl- and naphtenophenanthrenes. On the right side (b) we show results for phenanthrenes and their benzene analogues.

All solvents gave the maximum yield of extraction at 6 hrs irradiation time and almost full extraction of phenanthrenes and their benzologues (pyrenes, chryzenes) were achieved using benzene. Very similar behavior was observed for the samples isolated from Noryo and Samgori fields, hence we do not include these results for brevity.

Previously molecular mass distribution curves have been obtained for the same samples [22]. On this basis we have now determined the number and length of alkyl groups in phenanthrenes and benzologues. We find that phenanthrene hydrocarbons in non-substituted phenanthrene form as well as in forms of mono-, di-, tri-, and tetrasubstituted alkyl phenathrenes, mononaphteno- and dinaphtenophenanthrenes are present. For pyrenes and chrysenes mono-, di- and tri-substituted derivatives are found. Thus, those hydrocarbons together with short alkyl substituents contain also a long alkyl substituent. Apart from alkylphenanthrenes, we have also found

hydrocarbons with short – monomethyl-, dimethyl-, trimethyl- and ethylphenanthrenes substituents.

We have obtained fluorescence and phosphorescence spectra of the extracted aromatic concentrates by variation of the incident light λ_{exc} wavelength by 5 nm–10 nm at 77 °K. More polycyclic hydrocarbons were revealed in far regions of the spectrum. The results are presented in Tables 3 and 4.

As we see from these Tables, clear set of fluorescence and phosphorescence spectra bands are observed – corresponding to phenanthrene structures. At the same time, intensive bands of naphthalene are seen in the wide range of the wavelengths. Presence of intensive bands characteristic for multicyclic aromatic structures is seen. They correspond to pyrene hydrocarbons (376, 380 and 381 nm); benzopyrenes (400, 410, 420 and 428 nm) and benzofluorene hydrocarbons (344 nm). Small amounts of chrysene, tetraphene and benzophenanthrene hydrocarbons are also observed.

At least three luminescent centers are seen in Tables 3 and 4, starting at 354, 356 and 359 nm; phosphorescence spectra show maxima at 471, 478, 494, 509 and 516 nm,

Table 3. Phosphorescence spectra in n-hexane at 77 °K results; λ_{exc} is the incident light wavelength; λ_{ph} represents peaks of bands in phosphorescence spectra; J_{rel} are relative intensities of peaks. Column 2 pertains to benzofluorenes, Columns 3–5 to phenanthrenes, column 6 to chrysenes and columns 7 and 8 also to phenanthrenes

λ_{exc} (nm)														
	λ_{ph}	J_{rel}	λ_{ph}	J_{rel}	λ_{ph}	J_{rel}	λ_{ph}	J_{rel}	λ_{ph}	J_{rel}	λ_{ph}	J_{rel}	λ_{ph}	J_{rel}
260	464	0.47	471*	1.00	478*	0.83	494*	0.30	503 ⁰	0.57	509*	0.68		
270		0.64	471*	1.00	478*	0.80	494*	0.34	503 ⁰	0.55	509*	0.56		
280		0.64	471*	1.00	478*	0.70	494*	0.14	503 ⁰	0.41	509*	0.41	516*	0.10
290	464	0.52	471*	1.00	478*	0.86	494*	0.20	503 ⁰	0.43	509*	0.48		
300			471*	1.00	478*	0.87	494*	0.31	503 ⁰	0.60	509*	0.77	516*	0.53
310			471*	0.96	478*	1.00	–	–	–	–	–	–	518*	0.20
320	464	1.00					–	–	–	–	–	–	–	–

Table 4. Fluorescence spectra in n-hexane at 77 °K results. Symbols as in Figure 3

λ_{exc} (nm)																					
	λ_{fl}	J_{rat}	λ_{fl}	J_{rat}	λ_{fl}	J_{rat}	λ_{fl}	J_{rat}	λ_{fl}	J_{rat}	λ_{fl}	J_{rat}	λ_{fl}	J_{rat}	λ_{fl}	J_{rat}	λ_{fl}	J_{rat}	λ_{fl}	J_{rat}	
260	328	0.23	344	0.40	354*	1.00			372 ⁰	1.00					391*	0.53	413*	0.23			
270	328	0.38	344	0.38	354*	1.00			372*	0.90					391*	0.42					
280	328	0.54	344	0.58	354*	1.00			372*	0.83					391*	0.39	413*	0.14			
290	328	0.41	344	0.57	356*	1.00			372*	0.71					391*	0.15					
300	328	0.40	344	0.54	354*	1.00			372*	0.90					391*	0.40	413*	0.12			
310	328	0.42	344	0.83	359*	1.00			375*	0.82					393*	0.40					
320			344	0.85	356*	0.83	363	0.89	376*	1.00	380 ⁰	0.97	386 ⁰	0.69	396 ⁰	0.54					
325							365	0.64	377 ⁰	1.00	381 ⁰	0.93	388 ⁰	0.71	396 ⁰	0.63					
330					354*	0.47			379 ^A	1.00	382 ^A	0.50	387 ^A	0.47	398 ^A	0.50					
335									376 ^A	0.86	381 ^A	1.00	386 ^A	0.63	390 ^A	0.49	396 ^A	0.67			
340									376 ^A	1.00	380 ^A	0.94	387 ^A	0.81	397 ^A	0.83					
345											381 ^A	1.00			390 ^A	0.34	400 ^A	0.50			
350											381 ^A	1.00			391 ^A	0.48	400 ^A	0.61			
355											381 ^I	1.00					403 ^I	0.54			
360											381 ^I	1.00					405 ^I	0.66			
370															397 ^I	1.00			418 ^I	0.6	
375																	400 ⁺	1.00	422 ⁺	0.2	
380																	410 ⁺	1.00	432 ⁺	0.18	
390																			420 ⁺	1.00	
400																				428 ⁺	1.00
	Naphthalenes		Benzo-fluorenes		Phenanthrenes*		Chrysenes		3,4-Benzophenanthrenes ^o Pyrenes ^A Tetraphenes/Phenanthrenes*				Phenanthrenes* Benzopyrenes ⁺		Pyrenes ^A Tetraphenes/						

those maxima correspond to the first two centers. We infer the presence of di- and trisubstituted phenanthrenes in the positions 9 and 10.

Furthermore, we have used the luminescence spectroscopy to analyze the narrow aromatic concentrates at room temperature. The samples were isolated from Mirzaani field petroleum following a well established procedure [23]: sample 1 was extracted by hot (70 °C) benzene (410 °C–425 °C fraction); samples 2 and 3 extracted by hot (70 °C) benzene of upper and lower zones (460 °C–475 °C fraction) (Figure 2); samples 4 and 5 were extracted by dioxane from upper and lower zones (460 °C–475 °C fraction) (Figure 3). The measurements were carried out in 1.0 cm thick quartz cell at room temperature (25 °C ±1 °C).

The luminescence spectra show primarily phenanthrene hydrocarbons peaks at the wavelengths $\lambda_{max} = 255$,

270, 298 and 340 nm. Around λ_{max} between 325 nm and 330 nm we see also small trace peaks corresponding to naphthalene hydrocarbons.

We have studied also dependence of the luminescence of solvent (n-hexane) on the length of incident light. No significant effects were found.

Assuming a proportional relationship between the phenanthrene sample concentration C_{phen} and the maximum peak intensity, for the samples 1, 2 and 3 defined above we find:

$$C_{phen}(1) > C_{phen}(2) > C_{phen}(3) \quad (1)$$

As we see from the luminescence spectra in Figure 3, samples 4 and 5 contain mostly one type of aromatic hydrocarbons each.

In aromatic concentrates isolated from Mirzaani oil we have identified phenanthrene, fluorene and polycyclic

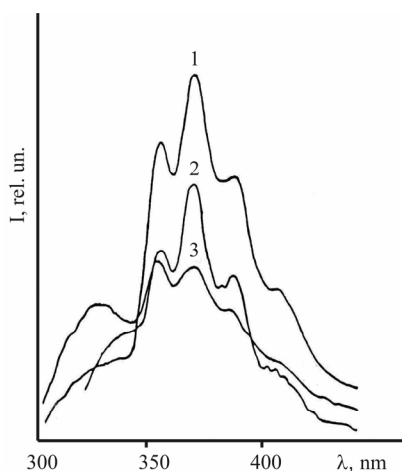


Fig. 2. Luminescence spectra of 1–3 Samples at the concentration $C = 10^{-5}$ g/ml and $\lambda_{exc} = 270$ nm

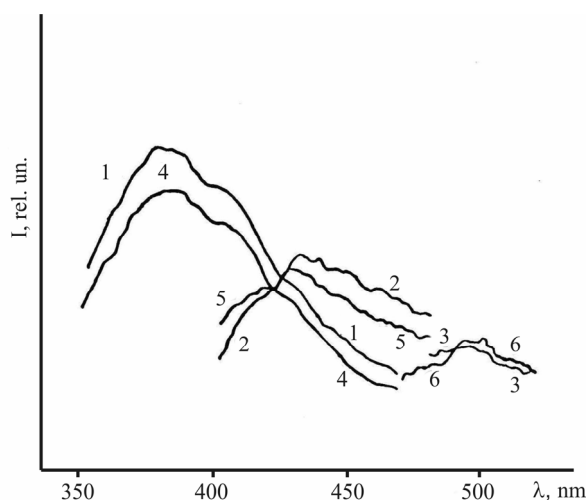


Fig. 3. Luminescence spectra of Sample 4 for various wavelengths: 1 for $\lambda_{exc} = 340$ nm, 2 for $\lambda_{exc} = 385$ nm, 3 for $\lambda_{exc} = 435$ nm. Sample 5: 4 curve for $\lambda_{exc} = 340$ nm, 5 for $\lambda_{exc} = 385$ nm, 6 for $\lambda_{exc} = 435$ nm. The concentration $C = 10^{-5}$ g/ml

aromatic hydrocarbons. The present results agree well with much earlier data obtained by gas-liquid chromatography [24], UV spectrophotometry [23] and mass-spectrometry [22].

UV absorption spectra of the samples were now recorded in the 200 nm–350 nm wavelength range using n-hexane as the solvent. We have also applied UV spectrophotometry to benzene eluates extracted from the following petroleum fractions: 498 °C–510 °C Noryo, 460 °C–475 °C Mirzaani and 450 °C–500 °C Samgori. The 498 °C–510 °C fraction was separated from Noryo oil by vacuum-distillation of aniline extract; fractions 490 °C–505 °C of Mirzaani oil and 450 °C–500 °C of Samgori oil were obtained by vacuum-distillation of crude oils – with the boiling temperatures recalculated for the 1 atm pressure. In Noryo oil we have found the AH content in the range (57–76) wt. %, in Mirzaani oil (64–70) wt. %, and in Samgori oil (47–55) wt. %.

A combined gas chromatography + mass spectrometry (GC/MS) method was used to study extracts of hot (70 °C)

benzene from the aromatic fraction of Noryo oil. Various types of mono-, di- and trimethyl-derivative AHs were identified, including: phenanthrene; 1-, 2-, 3-, 9-methyl-, 9-ethyl-, 9-propyl-, 9-isopropyl-, 9-butyl-phenanthrenes; 2,3-, 2,5-, 2,7-, 4,5-, 9,10-dimethylphenanthrenes; 1-methyl-7-isopropyl-, cyclohexyl-, three isomers of trimethylphenanthrenes; dimethylnaphtho-, dimethyldinaphtho-, butylnaphtho-, butyldinaphtho-phenanthrenes and chrysene.

4. CONCLUSIONS

To provide a broader perspective on our results, consider the stage at which maleic anhydride is used. MAH has quite a variety of applications [25–30]; clearly it is a very versatile compound. In our case PAHs react with MAH – an important stage followed by photodecomposition and extraction stages. Our method of determination of PAHs is less time consuming than LLE and also involves smaller amounts of volatile solvents. As noted by Lucas and her colleagues [9], PAHs have relatively high molar masses. Therefore, they also have relatively high boiling points. Our method can be used effectively for high-boiling point PAHs, for crude petroleum, for petroleum fractions and for petroleum-derived products such as lubricating oils after use.

Acknowledgments

Discussions with: Michael Bratychak, Lvivska Politechnika National University; Victor M. Castaño, National Autonomous University of Mexico, Queretaro; Elizabete F. Lucas, Federal University of Rio de Janeiro; and with other members of the Academy of Petroleum and Natural Gas, Kyiv, are appreciated. Partial financial support was provided by the Georgian Research and Development Foundation (GRDF), Tbilisi, and by the Robert A. Welch Foundation, Houston (Grant # B-1203).

REFERENCES

1. Andziulis, A., Andziulienė, B., Kindurys, A. Benzene Homologues Series in NMR Spectra of Blended Naptha *Materials Science (Medžiagotyra)* 8 2002: pp. 120–125.
2. Andziulis, A., Steponavicius, R., Kindurys, A., Abrickaja, V. Use of IR Spectroscopy for Identification of High-octane Olefins in FCC Naptha *Materials Science (Medžiagotyra)* 8 2002: pp. 522–526.
3. Shevchuk, V., Macyak, O., Babyak, L. Obtaining High Octane Components by Conversion of Hydrocarbon Raw Material on High-silica Zeolites *Chemistry & Chemical Technology* 1 2007: pp. 41–44.
4. Bratychak, M., Brostow, W., Pietkiewicz, D., Topilnitskij, P. Polyesters on the Basis of Petroleum Resin and Polyethylene Glycols *Chemistry & Chemical Technology* 1 2007: pp. 155–160.
5. Lorek, A., Paczusi, M. Studies on Sedimentation of Asphaltene Deposits in Distillation Residues *Chemistry & Chemical Technology* 1 2007: pp. 165–173.
6. Middea, A., Monte, M. B. M., Lucas, E. F. The Influence of the Solvent Medium on the Aggregation of Asphaltene Macromolecules and Determination of Their Molar Mass *Chemistry & Chemical Technology* 2 2008: pp. 91–97.

7. **Vieira, L., Lucas, E.** The Influence of Pressure and Dissolved Gases in Petroleum on the Efficiency of Wax Deposition Inhibitors *Chemistry & Chemical Technology* 2 2008: pp. 211–215.
8. **de Mello, M., Lucas, E.** Characterization and Selection of Polymers for Future Research on Enhanced Oil Recovery *Chemistry & Chemical Technology* 2 2008: pp. 295–303.
9. **Lucas, E. F., Mansur, C. R. E., Spinelli, L., Queiros, Y. G. C.** Polymer Science Applied to Petroleum Production *Pure & Applied Chemistry* 81 2009: pp. 473–494.
10. **Pyshyev, S., Lazorko, O., Bratychak, M.** Oxidative Processing of Light Oil Fractions *Chemistry & Chemical Technology* 3 2009: pp. 77–81.
11. **Vieira, L., Lucas, E.** The Influence of Pressure and Dissolved Gases in Petroleum on the Efficiency of Wax Deposition Inhibitors *Chemistry & Chemical Technology* 2 2008: pp. 211–215.
12. **Pyshev, S., Lazorko, O., Bratychak, M.** Temperature and Water Effects on the Oxidative Desulphurization of Straight-run Diesel Fraction with a High Sulphur Content *Chemistry & Chemical Technology* 3 2009: pp. 163–168.
13. **Jaramillo, P., Griffin, W. M., Matthews, H. S.** Comparative Life Cycle Air Emissions of Coal, Domestic Natural Gas, LNG, and SNG for Electricity Generation *Environmental Science & Technology* 41 2007: pp. 6290–6296.
14. **Jaramillo, P., Griffin, W. M., Matthews, H. S.** Comparative Analysis of the Production Costs and Life-cycle GHG Emissions of FT Liquid Fuels from Coal and Natural Gas *Environmental Science & Technology* 42 2008: pp. 7559–7565.
15. **Zolotov, M., Shock, E.** Abiotic Synthesis of Polycyclic Hydrocarbons on Mars *Journal of Geophysical Research* 104 1999: p. 14033.
16. **Grundl, T. J., Aldstadt III, J. H., Harb, J. G., St. Germain, R. W., Schweitzer, R. C.** Demonstration of a Method for the Direct Determination of Polycyclic Aromatic Hydrocarbons in Submerged Sediments *Environmental Science & Technology* 37 2003: pp. 1189–1197.
17. **Considine, T., Robbatt Jr., A.** On-site Profiling and Speciation of Polycyclic Aromatic Hydrocarbons at Manufactured Gas Plant Sites by a High Temperature Transfer Line, Membrane Inlet Probe Coupled to a Photoionization Detector and Gas Chromatograph/Mass Spectrometer *Environmental Science & Technology* 42 2008: pp. 1213–1220.
18. **Offenberg, J. H., Eisenreich, S. J., Chen, L. C., Cohen, M. D., Chee, G., Prophete, C., Weisel, C., Liroy, P. J.** Persistent Organic Pollutants in the Dusts that Settled Across Lower Manhattan after September 11, 2001, *Environmental Science & Technology* 37 2003: pp. 502–508.
19. **Charkviani, T. N.** Characteristics of Mirzaani Oil *Proceedings of Petre Melikishvili Institute of Chemistry* 15 1961: pp. 227–233.
20. **Topuridze, L., Khitiri, G., Melikadze, L.** Investigation of Signori Oil *Proceedings of Georgian Academy of Science – Chemistry* 5 1979: pp. 63–66.
21. **Köhler, A., Wilson, J. S., Friend, R. H.** Fluorescence and Phosphorescence in Organic Materials *Advanced Engineering Materials* 4 2002: pp. 453–459.
22. **Lekveishvili, E., Tevdorashvili, M., Kartvelishvili, E., Edilashvili, I., Polyakova, A.** Study of Composition and Structure of Phenantrene Hydrocarbons of Some Georgian Oils *Georgia Chemical Journal* 6 2006: pp. 506–510.
23. **Marushkevich, V., Kozlova, G., Lekveishvili, E., Tevdorashvili, M.** Luminescence Spectra Study of Aromatic Hydrocarbons High-boiling Fractions of Mirzaani Oil *Bulletin of the Georgian Academy of Sciences* 132 1988: pp. 517–520.
24. **Melikadze, L., Lekveishvili, E., Tevdorashvili, M., Japaridze, K.** Isolation and Study of Phenantrene Hydrocarbons from High-boiling Fractions Oily Fractions of Mirzaani Oil by Photocondensation with Maleic Anhydride. *Bulletin of the Georgian Academy of Sciences* 119 1985: pp. 309–312.
25. **De Brouwer, H., Schellekens, M. A. J., Klumperman, B., Monteiro, M. J., German, A. L.** Controlled Radical Copolymerization of Styrene and Maleic Anhydride and the Synthesis of Novel Polyolefin-based Block Copolymers by Reversible Addition-fragmentation Chain-transfer (RAFT) Polymerization *Journal of Polymer Science Chemistry Part A: Polymer* 38 2000: pp. 3596–3603.
26. **Yua, J., He, J.** Crystallization Kinetics of Maleic Anhydride Grafted Polypropylene Ionomers *Polymer* 41 2000: pp. 891–898.
27. **Chow, W. S., Bakar, A. A., Ishak, Z. A. M., Karger-Kocsis, J., Ishiaku, U. S.** Effect of Maleic Anhydride-grafted Ethylene–Propylene Rubber on the Mechanical, Rheological and Morphological Properties of Organoclay Reinforced Polyamide 6 + Polypropylene Nanocomposites *European Polymer Journal* 41 2005: pp. 687–696.
28. **Vilenskyy, V., Brostow, W., Pietkiewicz, D.** ICh-spektroskopichne doslidzhennya osoblivostei himichnogo modifikuvannya kopolimeru stirol-maleinovyi angidrid 3,5-bis(trifortmetyl)anilinom *Polimernyi Zhurnal* 27 2005: pp. 242–248.
29. **Ye, P.; Xu, Z.-K.; Wu, J.; Innocent, Ch., Seta, P.** Nanofibrous Poly(acrylonitrile-co-maleic acid) Membranes Functionalized with Gelatin and Chitosan for Lipase Immobilization *Biomaterials* 27 2005: pp. 4169–4176.
30. **Orozco, V. H., Brostow, W., Chonkaew, W., Lopez, B. L.** Preparation and Characterization of Poly(lactic acid)-g-maleic Anhydride + Starch Blends *Macromolecular Symposia* 277 2009: pp. 69–80.

DOI: 10.5755/j02.ms.26064