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Modifying the Coal of the Sergeevo Deposit by Means of Liquid-Phase Catalytic Alkylation with Isopropyl Alcohol

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Abstract

Modifying the low-calorific lignite from the Sergeevo deposit by means of liquid-phase catalytic alkylation with isopropyl alcohol was performed. The basic processes involved in the interaction of the coal under investigation with isopropyl alcohol were described. A positive effect of the alkylation treatment exerted on the coal bituminosity, the componential composition and the physicochemical characteristics of modified products obtained has been revealed.

Key words: alkylation, isopropyl alcohol extraction, bitumen, waxes, lignite

INTRODUCTION

The obtaining of soluble products from solid fuels with a sophisticated multi-component composition is of great importance for the study and practical use of the huge reserves of naturally occurring organic raw materials. One of the ways to improve the efficiency of the extraction processing of coal consists in the preliminary alkylation thereof with low-molecular alcohols [1, 2]. The resulting modified products exhibit improved chemical and technological characteristics and, alongside with a wide application as target products they represent a promising raw material for further chemical processing using the methods of extraction, hydrogenation, obtaining ash-free fuels, etc. The present work is devoted to the application of the alkylation technique in order to produce modified waxes from brown coal of the Sergeevo deposit. We studied the transformation of the organic matter of coal in the course of the reaction with carbon with isopropyl alcohol as well as the influence of the alkylation upon the yield and the composition of extraction products.

EXPERIMENTAL

The subject of inquiry was presented by coal taken from the Sergeevo deposit (Amur Region) being of interest for chemical processing [3, 4]. Coal characteristics: $W^a = 8.1\%$, $A^a = 22.3\%$, the mass fraction of benzene bitumen 15.1, that of humic acids 69.7 % (daf); elemental composition, (% daf): C 66.1, H 5.5, N 0.7, S 0.4, O 27.3; atomic ratio H/C = 1.0. As an alkylating agent we used isopropyl alcohol (IPA). Not having high activity in the esterification reactions, isopropanol is used for the preparation of macromolecular synthetic esters of fatty acids [5–8] and modified waxes from solid fuels [9].

The alkylation was carried out using a steam bath during 4 h at a ratio of carbon/solvent = 1 : 20; the catalyst used represented 7 % H_2SO_4 solution in isopropyl alcohol. The flowchart of separating and studying the reaction products is demonstrated in Fig. 1. After the reaction, the resulting mixture was cooled and centrifuged. The solid and liquid phases were washed with water and the catalyst was dried in a vacuum oven at 70 °C until reaching constant mass.

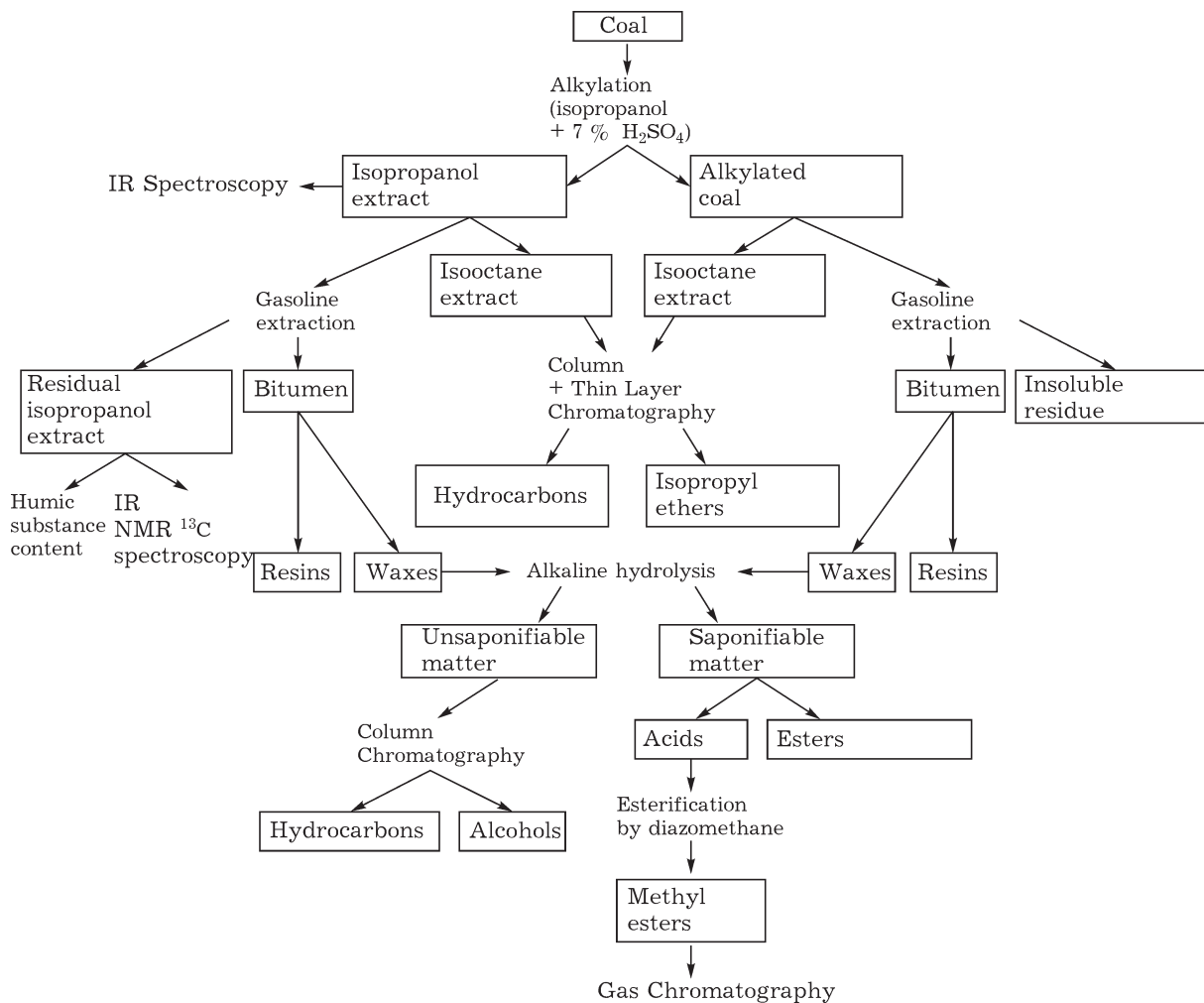


Fig. 1. Schematic diagram of coal processing and investigation *via* alkylation.

Alkylated carbon (AC) and the isopropanol extract (IPE-A) were used for extracting bitumen species soluble in gasoline by means of the Graefe's method, which bitumen species were separated into resins and waxes *via* repeated extraction with diethyl ether in the course of cooling. In the residual (without bitumen) isopropanol extract (RIPE-A) we determined the content of humic substances according to the State Standard GOST 9517-76. Under similar conditions, the coal was extracted with isopropyl alcohol with no catalyst to obtain the following products: isopropanol extract (IPE), residual carbon (RC) and residual (after extracting the bitumen species) isopropanol extract (RIPE).

The group composition of deresined wax was determined by means of alkaline hydrolysis by 1 M KOH solution in alcohol. Unsaponifiable components were separated into hydrocar-

bon and alcohol fractions with the use of column chromatography on a "Durasil H" silica gel (column diameter 1 cm, the height of the adsorbent bed 80 cm). The sampling of the fractions was carried out *via* successive elution by octane and, residual components were removed by benzene. Saponifiable fractions were converted into methyl esters *via* esterification by diazomethane with further separation the compounds of normal structure by means of adding with urea.

The analysis of the individual composition of fatty acid methyl esters was carried out by means of gas chromatography (GC) with the use of an Agilent 6890N chromatograph with a flame ionization detector using a HP-5 capillary column (30 m × 0.25 mm × 0.25 μm) under the conditions of temperature programming from 100 °C (2 min exposure) at a rate of 10 °C/min

up to 340 °C (2 min exposure). The evaporator temperature was equal to 320 °C, that of detector being of 360 °C. Helium was used as a carrier gas, with a constant flow amounting to 2 mL/min. Sample injection was performed in a splitless mode, sample volume being of 1 μ L. A Supelco 47885-U 37-componential mixture of fatty acid methyl esters was used as the reference.

Solid products (AC) and liquid products (IPE-A) resulted from the modification were subjected to treatment by isooctane in a Soxhlet apparatus, whereas the extracts obtained were separated by means of column chromatography into ester and hydrocarbon fractions. As the adsorbent we used a "Durasil H" silica gel, whereas cyclohexane and 5 % solution of diethyl ether in cyclohexane, respectively, were used as eluents. The identification of hydrocarbons and esters was performed by means of thin layer chromatography (TLC) using Sorbfil UV-254 plates in solvent system benzene/ethyl acetate (95 : 5); a mixture of *n*-alkanes C_{14} – C_{16} (R_f 0.86) and isopropyl myristate (R_f 0.70) being used as reference. The visualization of the chromatographic traces was carried out via spraying by a 10 % solution of sulfuric acid in ethanol and subsequent annealing the plates. It was revealed that the cyclohexane fractions of liquid and solid alkylation products are presented by hydrocarbons (R_f 0.86), whereas the fractions eluted with a mixture of cyclohexane and 5 % of diethyl ether, contain fatty acids, isopropyl esters (R_f 0.70) and, to all appearance, naturally occurring esters (R_f 0.50). At the same time, the chromatograms of similar products obtained without catalyst did not exhibit any isopropyl esters to be identified.

The quantitative ^{13}C NMR spectra were registered using a Varian-VXR500S NMR spectrometer with the operating frequency of 125.6 MHz in 1 % NaOD solution.

Infrared spectra were registered by means of a Perkin-Elmer Spectrum One spectrometer equipped with an attenuated total reflection unit using the tableting with KBr.

RESULTS AND DISCUSSION

The basis of the catalytic alkylation of solid fuels by low molecular mass alcohols is pre-

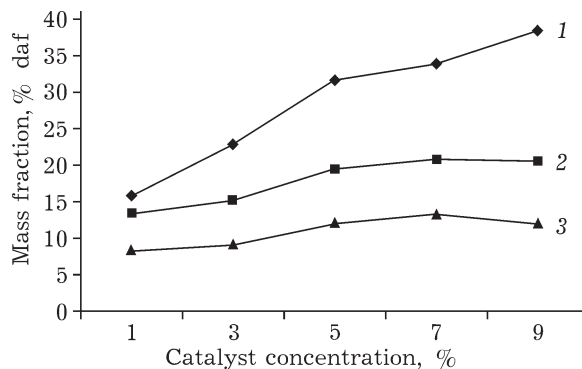


Fig. 2. Yield of alkylation products depending on the catalyst concentration: 1 – isopropyl extract, 2 – bitumen, 3 – waxes.

sented by the esterification reaction that consist in the formation of esters in the presence of strong acids. In the course of preliminary testing for optimizing the concentration of catalyst the alkylation of the Sergeevo coal was the carried out in the presence of 1, 3, 5, 7 and 9 % sulphuric acid solution in isopropyl alcohol. According to the data obtained (Fig. 2), increasing the amounts of catalyst up to 7 % results in increasing the coal solubility as well as in the content of waxes and bitumen species in the reaction products. Further increasing the concentration results in an only slight increase in the yield of bitumen, and in decreasing the content of waxes, in reducing the dropping temperature and the saponification number thereof (Fig. 3). In this case, there is possibility of an undesirable oxidation of unsaturated coal components. In this regard, the alkylation of the Sergeevo coal with isopropyl alcohol recognized to be optimal within the concentration range of the catalyst equal to 5–7 %, and the further studies were carried out in the presence of 7 % sulphuric acid solu-

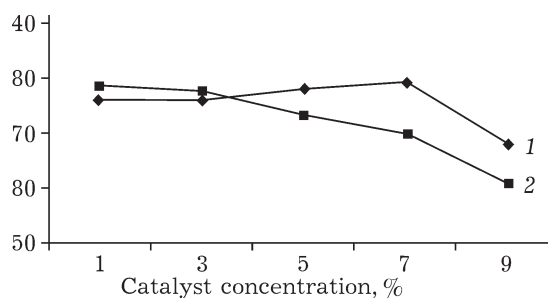


Fig. 3. Physicochemical characteristics of waxes depending on the catalyst concentration: 1 – dropping temperature, °C; 2 – saponification number, mg KOH/g.

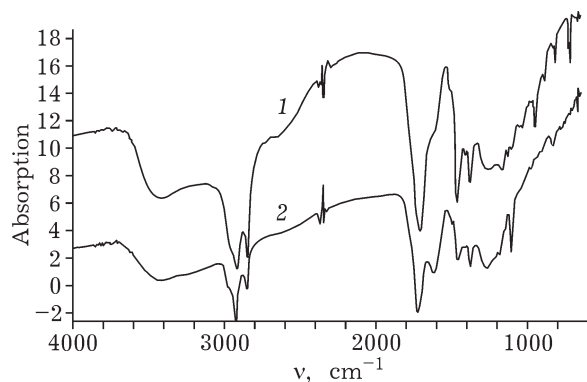


Fig. 4. IR spectra of soluble products obtained without catalyst (1) and in the presence thereof (2).

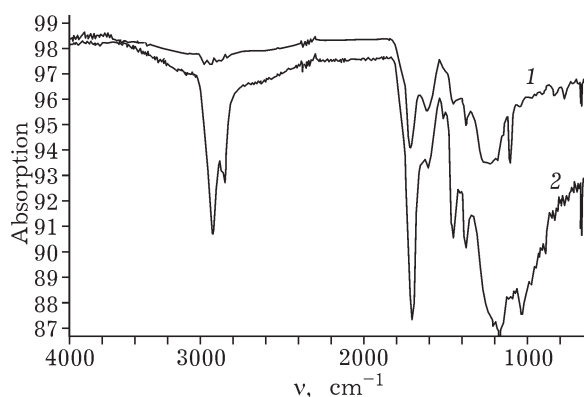


Fig. 5. IR spectra of residual (with no bitumen) isopropanol extracts obtained in the presence of catalyst (1) and with no catalyst (2).

tion, which provides a higher yield of liquid products.

Under the extraction conditions without catalyst with the use of isopropyl alcohol the Sergeevo coal exhibits the extraction of naturally occurring components those are presented (Fig. 4, curve 1) by aliphatic structures (2920, 2860, 1460, 1380, 720 cm^{-1}) those are bound with different functional groups of fatty acids (1710, 1270 cm^{-1}), alcohols (3420, 1030 cm^{-1}), esters (1165 cm^{-1}) and aromatic compounds (950, 820 cm^{-1}). Soluble alkylation products (see Fig. 4, curve 2) are enriched with carboxylic (1720, 910 cm^{-1}) carbonyl (1275, 1220 cm^{-1}), phenolic (1250 cm^{-1}) groups, bound with unsaturated (1615 cm^{-1}) aromatic (825, 770, 690 cm^{-1}) and short saturated groups (prevailing absorption band 1380 cm^{-1}). In the presence of the catalyst (under the alkylation conditions), a more complete extraction of bitumen species is achieved alongside with increasing the carbon solubility (Table 1). This is indicated by an abrupt de-

crease in the absorption of the aliphatic groups within the range of 2920–2860 cm^{-1} and 1460 cm^{-1} in the IR spectrum of the residual (after the removal of bitumen) isopropanol extract (Fig. 5, curve 1) as compared with that obtained without catalyst (curve 2).

Basing on data concerning the polyfunctional composition of RIPE-A confirmed by the results of ^{13}C NMR spectroscopy (see Table 2), and the complete solubility thereof in 1% sodium hydroxide solution and in ethanol one could propose that, alongside with the bitumen species, the source of increasing the content of liquid products in the course of interaction between the Sergeevo coal and isopropanol is presented by a water-soluble fraction of humic substances. To all appearance, the presence of the catalyst facilitates the demineralization of the coal and the liberation of the acids of different chemical nature (humic, resin, wax, etc.) bound in the form of salts, which is supported by an increase in the concentration of

TABLE 1

Characteristics of alkylation products

Samples	Yield, % daf	Content, % daf				Group composition of waxes, %			
		Bitumen	Waxes	Resins	Humic acids	Unsaponifiable cpds	Saponifiable	Esters	
						HC	Alcohols		
<i>Coal treated with IPS in the absence of catalyst</i>									
IPE	15.4	8.5	4.5	4.0	—	7.3	5.2	41.6	45.9
RC	85.4	4.8	3.4	1.4	70.5	3.8	3.2	33.6	59.4
<i>Coal treated with IPS in the presence of 5% H₂SO₄</i>									
IPE-A	33.9	12.9	5.5	7.4	—	9.1	16.9	55.2	17.8
AC	71.1	8.0	7.8	0.2	76.1	5.2	7.0	9.6	78.2

TABLE 2

Fragmental composition parameters of residual isopropanol extracts (RIPE) from ^{13}C NMR spectra

RIPE	Carbon content in structural fragments, rel. %									f_a
	C=O	C _{quin}	COOH	C _{ar} O	C _{ar} + CH _{ar}	C _{alk} O	CH ₃ O	C _{alk}		
Without catalyst	1.02	1.12	3.87	5.27	20.45	4.51	1.97	58.80	25.72	
With catalyst	8.21	2.19	9.90	7.74	28.93	9.65	2.75	30.63	34.60	

TABLE 3

Physicochemical characteristics of alkylation products

Parameters	Initial coal				Modified coal			
	IPE		RC		IPE-A		AC	
	Waxes	Resins	Waxes	Resins	Waxes	Resins	Waxes	Resins
Acid number, mg KOH/g	35.3	52.5	30.8	–	41.6	63.9	25.7	–
Saponification number, mg KOH/g	78.5	73.4	119.3	–	69.6	80.1	128.1	–
Dropping temperature, °C	76	–	80	–	79	–	83	–

humic acids in the alkylated coal, by increasing the acid number and the yield of resins, as well as the content of saponifiable components in the wax composition (see Tables 1, 3). The destruction of organo-mineral bonds occurring in this case is accompanied by extracting an additional amount of wax hydrocarbons.

Under the influence of the catalyst the acids liberated due to demineralization, alongside with free acids of the original coal are subjected to esterification with isopropanol. This is evidenced by an increase in the number of O-alk bonds (increasing the absorption intensity within the range of 1100 and 1270–1240 cm^{-1}) and by the formation of isopropyl ester revealed by means of TLC. However, under the condi-

tions chosen the isopropyl esters are predominantly formed in the course of the re-esterification reaction, which is indicated by decreasing the concentration of difficultly saponified esters as well as by the formation of a significant amount of alcohols (see Table 1) resulting from the substitution of a naturally occurring high molecular mass alcohol radicals by the radical of isopropyl alcohol. This is confirmed by shifting the IR spectral band at 1710 cm^{-1} corresponding to the carbonyl groups of the naturally occurring esters of high molecular mass carboxylic acids and long-chained alcohols towards the region of 1735 cm^{-1} , that is characteristic of esters with short-chained alcoholic substituents (see Fig. 4, curve 2).

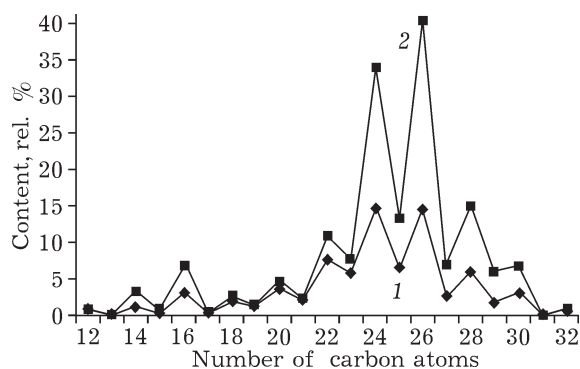


Fig. 6. Number of carbon atoms distribution for saponifiable acids of the isopropanol extract obtained without catalyst (1) and in the presence thereof (2).

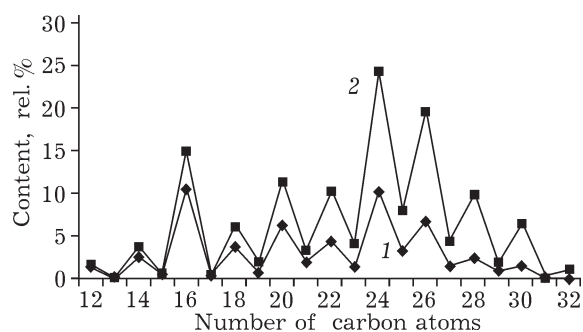


Fig. 7. Number of carbon atoms distribution for saponifiable acids: 1 – residual coal after extraction without catalyst; 2 – alkylated coal in presence of catalyst.

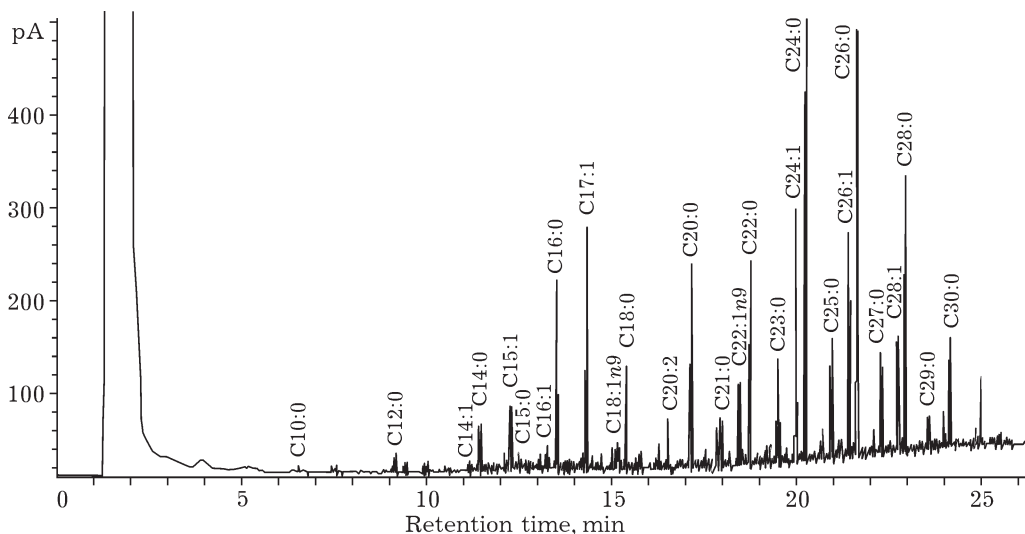


Fig. 8. Chromatographic profile of the saponifiable acids of alkylated carbon.

In the course of determining the group composition of the waxes, the esters obtained can be hydrolyzed in a more ready manner than native esters to serve as a source of the replenishment of the saponifiable fraction. Chain length distribution inherent in saponifiable acids contained in the liquid (Fig. 6) and in solid alkylation products (Figs. 7, 8), indicates that the participation of the catalyst promotes involving a significant amount of high molecular mass compounds in the process.

Increasing the yield of liquid products in the course of coal alkylation, as well as concentrating the resinous substances therein and increasing the fraction of readily hydrolyzed esters (see Table 1) results in enriching the alkylated coal by macromolecular esters those are resistant with respect to saponification, and in improving the physicochemical characteristics of the wax obtained such as increasing the dropping temperature and the saponification number (see Table 3). Thus, the bitumen species extracted from the AC are within 97.5 % presented by wax components and do not require any additional resin removing.

CONCLUSION

The modification of coal from the Sergeev deposit by means of a liquid-phase catalytic alkylation technique using isopropyl alcohol rep-

resents an effective method for increasing the yield of soluble products as well as increasing the bituminosity of coal. The presence of the catalyst initiates the process of coal demineralization, which is accompanied by the destruction of organic bonds and releasing the acids bound. The processes of esterification and re-esterification result in the formation of isopropyl esters which facilitates increasing the yield of wax fractions alongside with hydrocarbons, alcohols and acids. The characteristic feature of the interaction between coal under investigation and isopropanol consists in the fact that the main contribution to the formation of isopropyl esters is drawn by the reaction of re-esterification. The alkylated coal already at the stage of extracting the crude wax is an attractive feedstock for obtaining a product free of resinous substances to a considerable extent. The waxes of alkylated carbon are enriched with esters resistant with respect to saponification and they exhibit improved physicochemical characteristics.

REFERENCES

- 1 Zhrebtsov S. I., *KhTT*, 3 (2007)60.
- 2 Zhrebtsov S. I., Musin Yu. V., Moiseev A. I., *KhTT*, 4 (2009) 12.
- 3 Noskova L. P., Rokhin A. V., Sorokin A. P., *KhTT*, 3 (2007) 9.
- 4 Noskova L. P., *Chem. Sustain. Dev.*, 17, 1 (2009) 61.
URL: <http://www.sibran.ru/en/journals/KhUR>
- 5 Rogozinski M. J., *Gas Chromatogr.*, 2 (1964) 136.

6 RU Pat. No. 2165408, 2001.

7 Yalsinyuva T., Deliguz H., Boz I., Gьrkaуnak M.A.,
Int. J. Chem. Kinetics, 40, 3 (2008) 136.

8 Peuchant E., Wolff R., Salles C. and Jensen R., *Anal. Biochem.*, 181 (1989) 341.

9 Author's Certification No. 1675321 USSR, 1991.