ХИМИЧЕСКАЯ ТЕХНОЛОГИЯ. ХИМИЧЕСКАЯ ПРОМЫШЛЕННОСТЬ

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***B.K. Donenov*[1], *K.I. Imanbekov*[2], *Zh.N. Kainarbayeva*[3], *A.M. Joldassov*[3], *A. Kozybayev*[4]**

[1]Kazakh-British Technical University
[2]Institute of Chemical Sciences,
[3]Kazakh-British Technical University,
[4]Research Institute Food safety,
Almaty c., Kazakhstan

INDUSTRIALLY IMPORTANT RENEWABLE HYDROCARBONS IN THE GULF OF LAKE BALKHASH

Аннотация. Исследованы образцы липидов трех веществ оз. Балхаш - альгината микроводоросли, сапропеля и балхашита. Альгинаты не содержали никаких углеводородов, тогда как в образцах сапропеля и балхашита имеется их множество. Углеводороды состоят из смеси коротких и длинных цепей парафинов, олефинов и изопреновых соединений, в том числе ди-, три-, tetraterpanes, стеранов и ликопина. Экспериментально обнаруженные парафины и олефины являются производными образующихся жирных кислот, а смеси линейных и циклических терпеноидов связаны с каротинами, в процессе фотобиосинтеза культуры Botryococcus balkachicus. Природа появления возобновляемых углеводородов непосредственно связана с наличием благоприятных гидрологических условий для обильного роста этой культуры в данном заливе. Минеральный состав воды представлен следующим рядом последовательности: сульфаты > хлориды > карбонаты и имеет слабощелочной показатель pH=8,58.
Ключевые слова: балхашит, ботриококкус, возобновляемые углеводороды, липиды, сапропель.

Түйіндеме. Балхаш көліндегі үш заттың липидтерінің - балхашит, сапропел және микробалдырлар алгинатаның үлгісі зерттелді. Альгинаттардың құрамында парафин қатарындағы көмірсутектер жоқ болып шықты, ал сапро-

пел мен балхашитта олар көптеп кездеседі. Көмірсутектер парафин, олефин және изопрендік қоспаларының қысқа және ұзын тізбектерінің қосылыстарынан тұрады, сонымен қатар ди-, три-, tetraterpanes, стерандар мен ликопиндерден тұрады.Тәжірибелік мәліметтер көрсетуі бойынша парафиндер мен олефиндер туынды майлы қышқылдар болып табылады және Botryococcus balkachicus дақылдарының фотобиосинтез процесі кезіндегі сызықты және циклді терпеноид қоспалары каротиндерге байланысты. Қайта өңделетін көмірсутектердің пайда болу табиғаты осы дақылдың бұл шығанақта жақсы өсуі үшін қолайлы гидрологиялық шарттардың бар болуымен байланысты. Судың минералды құрамы келесі қатар бойынша сипатталады: сульфаттар > хлоридтер > карбонаттар және орташа сілтілікті көрсетеді pH=8,58.
Түйінді сөздер: балхашит, ботриококкус, жаңартылатын көмірсутектер липидтер, сапропель.

Abstract. Samples of three substances lipids of Lake Balkhash has been studied - alginate microalgae, sapropel and balhashit. Alginates don't contain any hydrocarbons, whereas the samples of sapropel and balhashit contain many of them.Hydrocarbons consist of a mixture of short and long chains of parrafins, olefins and isoprene compounds, including di-, tri-, tetraterpanes, steranes and lycopene.Experimentally detected paraffins and olefins are the derivatives of forming fat acids, and the mixtures of linear and cyclic terpenoids are connected with carotines, in the process of photobiosynthesis of Botryococcus balkachius culture. The nature of appearance of renewable hydrocarbons directly is connected with favorable hydrological conditions for a rich growth of this culture in a given gulf. The mineral composition of water corresponds to the following row of sequence: sulphates > chloride > carbonates and has a alkalescent indicator pH = 8.58.
Key words: balhashit, botriococcus, renewable hydrocarbons, lipids, sapropel.

1. **Introduction.** Due to the presence of special materials of Balkhashite [1], Balkhash region has been representing enormous industrial interest. Balkhashite is formed from degraded microalgae biomass of the Botryococcus braunii [2,3], which grows in the South-Western extremity of the lake, the Gulf of Ala-Kul. Calorific value of Balkhashite is higher than that of coal, and is comparable with the value of crude oil which is 37.69 J/kg.

Relationship between Balhashite formation and Botryococcus balkachicus is due to presence of the same hydrocarbons in both Botryococcus balkachicus biomass and Balhashite composition. However, the process of formation of Balhashite from Botryococcus balkachicus biomass hydrocarbons is not fully revealed yet. The basic assumption was that the accumulation of microalgae biomass takes place on the water surface. Then, the biomass is relocated to the coast by the waves where it eventually decomposes to combustible material of Balhashite.

Therefore, the study aimed to establish the current capacity of the lake as a source of renewable hydrocarbons is highly relevant and is of great industrial interest.

1. Research Methods

1.1. The study of the site. Currently, former Gulf of Ala-Kul is the separated from main lake because of the sharp reduction of water inflow to Lake Balkhash. Lake Ala-Kul is located in the South-Western tip of Lake Balkhash in Kazakhstan (Fig. 1).

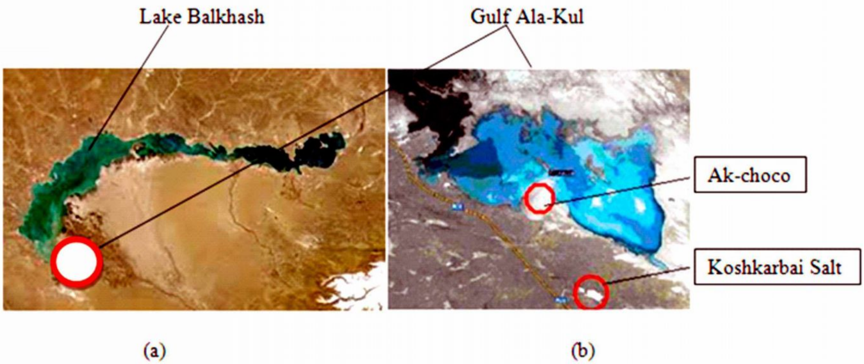


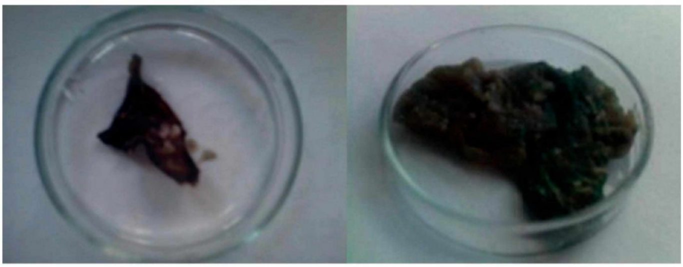
Fig.1 – Surface water of Lake Balkhash. a) Lake Balkhash and Gulf Ala-Kul. b) Place of sampling the Gulf Alakol of Lake Balkhash in 2012. Balkhashite and samples of microalgae biomass were taken from Ak-choco local. Sapropele was taken from Koshkarbai salt in 2012

Level of water in the lake undergoes periodic changes, which in turn leads to alteration of lake's surface. The water level has significantly increased in recent years, but the former water level has still to be reached. You can still see the accumulation of combustible material on the former bottom on the West coast of the Gulf.

The Balkhashite samples are shown in Figure 2. Figure 1 depicts the rise of water level in the last ten years, due to which, freshly formed samples of the Balkhashite cannot be observed [4].

Fig. 2 – Samples of Balkhashite were taken from seaboard of Gulf Ala-Kul in summer 2012. Samples have form pieces with 5 cm width 7 cm length, and the thickness of 0.3 to 1 cm.
(photo of our own data)

Observations of the water samples of the lake under the microscope have shown the presence of abundant colonies of strains of Botryococcus balkachicus, which verifies the fact that the microalgae is still in great shape and grows naturally (see Fig. 3). It was also observed that accumulated microalgae biomass was floating on the surface of the water.



(a) (b)

Fig. 3 – Dry (a) and wet (b) biomass of mixed microalgae's of gulf Ala-Kul. Samples of biomasses microalgae were grown in the photobioreactor during the periods July and August. Periods of the cultivation of biomass were up 50 days under the open sky in natural light corresponding to the solar intensity of not less than 400 MJ/m^2. The biomass was gelatinous. It is capable of absorbing water in the amount of 20-30 times of its own weight (photo of our own data)

2.2. Sampling. The following samples from the Gulf of Ala-Kul were selected as the objects of the research:

• Samples of Balkhashite collected from the shores of the Gulf on May 2012;

• A mixture of biomass (alginates) of natural cultures of the Gulf and the ones cultivated in the Laboratory;

• Sapropel – bottom deposition of the Gulf. Coordinates of water samples corresponds to the Northern Latitude – 440 87' and Eastern Longitude – 740 15', and bottom sediments correspond to Northern Latitude – 440 76', Eastern Longitude – 740 32'.

2.3. Laboratory studies. Complete analysis of the chemical composition of water and salt of Gulf of Ala-Kul, was conducted in the laboratory of analytical chemistry.

Biomass of mixtures of wild strain microalgae has been cultivated in 20-liter photo bioreactor made of a PET bottle using the natural water of the lake as a base. The nutrient medium supplied was the mixture of carbon dioxide and air, which was pumped into the reactor via the aquarium compressor with an average air supply speed of 4.5 l/min. Period of biomass cultivation was up 50 days under the solar intensity of not less than 400 MJ/m^2.

Microscopic studies of strains of cultures were conducted using the optical microscope with multiplicity resolution of 10, 20, 40 and 100.

The extraction was performed sequentially first in methanol, and then in petroleum ether.

Compositions of lipids have been determined by gas-liquid chromatography (GLC) and Mass-Spectrometric (MS) investigations. After careful washing and drying, Sapropel underwent the process of lipid extraction. The extraction was carried out in the methyl alcohol and petroleum ether followed by dissolution in hexane after which the resulting solutions were analyzed by the GLC and the MS. The output of the extract was up 1.06 grams for a kilogram sapropel with the humidity of 85%.

Balkhashite and Biomass have undergone pyrolysis at 600 ^{0}C and 450 ^{0}C, respectively, with the heating temperature speed of 10 ^{0}C per minute in presence of nitrogen. The lipid output was 72 milliliters for 150 grams of Balkhashite with humidity of 7 %. Lipids were dissolved in hexane.

Extracts of Sapropel and pyrolisis oil of Balkhashite have been analyzed using GLC with mass spectrometer detector. Solutions of lipids underwent centrifugation for 7 minutes at 3000 rpm, and 25 ml sample was taken from top layer of a solution immediately after the stoppage. Selected dose was immediately injected into the mass-spectrometric detector.

Chromatograph conditions: Method EPA 8270, minutes mass Range: 30-500 inch m/e. Ionization energy 70 eV, the temperature of the ion source 290 ^{0}C, speed of flow of the carrier gas is 1 ml/min. GLC devices of "Agilent Technologies" were used in all cases.

MS studies of the pyrolysis of the oils obtained from samples of Biomass and Balhashite were conducted by using Solariks 7T (Bruker Daltonics) device.

3. The results of the study

3.1. **Physicochemical parameters of the water.** The results of the chemical analysis of the water from Gulf of Ala - Kul of Balkhash Lake, are presented in table 1. The water in the Gulf was average alkaline, with a pH = 8.58. Total mineralization's of the water varies depending on the season: in the beginning of summer it reaches about 3 g/l, and by the end of summer there is an increase up to 7 g/L. Mineral content of the water of the Bay is characterized by a high content of sulfate ions. Characteristic feature of the composition of the water in the Gulf of Ala-Kul (Balkhash), where intensive growth of Botryococcus balkachicus culture was observed, is the fact that the ratio of anion sulphate to chloride anion reaches 1.45; the ratio of the anion sulfate to anion carbonate reaches a value of 2.64; and the ratio of chloride to carbonate is 1.84. Therefore, the chemical composition of the waters of the gulf of Ala-Kul can be arranged in the following sequence: sulphate > chloride > carbonate.

Cation content in water of the gulf of Ala-Kul is presented in table 2. Contents of Na+ substantially prevail over all other components. The multiplicity of excess reaches from 4 to 14 times.

Table 1

Characteristics of the waters of the Gulf of Ala-Kul of Lake Balkhash

Gulf	pH	Content of salt, g/l	CL^-, g/l	SO_4^-, g/l	HCO_3^- g/l	SO_4/CL^-	SO_4^-/HCO_3^-	Cl^-/HCO_3
Ala-Kul	8,58	2,97-7,0	0,6825	0,9796	0,372	1,4353	2,633	1,835

The second most abundant cation was found to be Mg, and the contents K+, Ca+ were roughly equal. The ratio of Na+ to the other cations is the following: Na+ / Mg = 4.24; Na+ / K+ = Na+ / Ca+ = 14.2; Na+ / NH4 = Na+/ Fe = 6 800.

Table 2

Content of cations in water of the Gulf of Ala-Kul

Cations, mg/dm^3	Na^+	K+	Ca^+,	Mg^{++}	NH_4	Fe^{+2}	Fe^{+3}	total
Ala-Kul	680,0	47,6	48,0	160,5	0,1	<0.1	< 0.1	936,3

3.2. **Phytoplankton divisions and species.** Abiotic and other favorable climatic conditions are not the only requirements, which ensure a rapid growth of different species of microalgae in Ala-Kul gulf. For example, the number of sunny days is 130 per year, with light energy of 15.9 $MJ/m^2/day$. The temperature on the surface of the water varies from 0 0C in December to 280 C in July. The lake is covered with ice in November, which melts down in early April.

Fig.4 presents the pictures of the different strains of microalgae, which grow in the gulf. Microalgae can be classified into three different groups: diatom – Bacillariales (Amphora, Chaetoceros, Compilodiscus sp.); blue-green – Cyanophyta (Chroococcus minor Nag. Oscillatoria sp., Gomphosphaeria aponina, Isocytis messanensis, Phormidium Retzii); and green - Chlorococcophyceae (Botryococcus balkachicus, Cladophora, OocystissolitariaWittr.).

Diatoms have been commercially important due to the high value edibility characteristics, caused by a high content of polyunsaturated fatty acids and the proteins. Its main usage lies in the production of

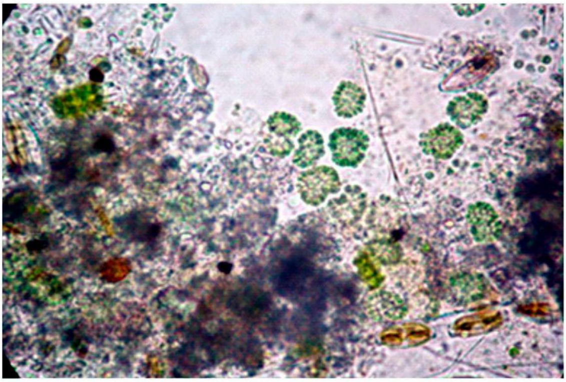


Fig. 4 – Population of micro-algae, the South-Western part of lake Balkhash (photo of our own data)

the essential fatty acids of the omega-3. This technology is commercially viable and comparable with products derived from fish oil. Essential fatty acids have high market demand and therefore, the creation of their industrial base is extremely important.

Cyanobacteria (blue-green) are rich in the biologically active compounds that possess antiviral, antibacterial, and antifungal actions. Moreover, most of these bioactive compounds belong to the so-called lip peptides, i.e. compounds composed of amino acid fragments associated with the fatty acid residues. Many of them have found practical application in aquaculture, wastewater treatment, food products, fertilizers and production of secondary metabolites including exopolysaccharides, vitamins, toxins, enzymes and pharmaceuticals.

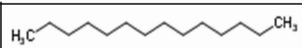
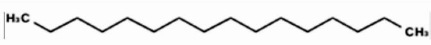
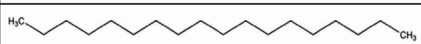
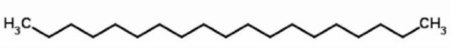
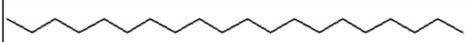
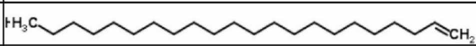
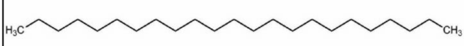
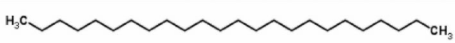
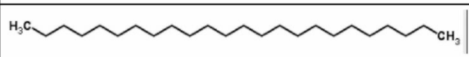
Botryococcus balkachicus (see Fig. 3) carries the main interest among the green microalgae of gulf of Ala-Kul. Content of the lipids can be in the range from 2% to 75% of dry biomass. Lipid formulations consist of groups of polar and non-polar lipids, as well as hydrocarbons.

3.3. **Lipids.** The results of GLC studies of lipid samples of Sapropel and Balkhashite, as well as MS studies of the oil samples of Biomass and Balkhashite are presented in Figure 5. The results of their identification are showed in Table 3 (a,b), Table 4.

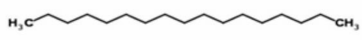
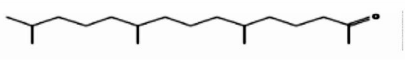
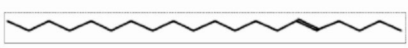
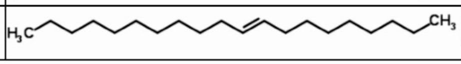
Table 3

Identification compositions by method GLC: a) of Sapropel extracts; b) Balchashite oil

Table 3a

№	Chemical formula	Structure	%
Extract of methyl alcohol			
1	Tetradecane $C_{14}H_{30}$		4,56
2	Pentadecane $C_{15}H_{32}$		6,21
3	Hexadecane $C_{16}H_{34}$		15,87
4	Octadecane $C_{18}H_{38}$		29,40
5	Nonadecane $C_{19}H_{40}$		6,76
6	Eicosane $C_{20}H_{42}$		3,41
7	Heneicosane $C_{21}H_{44}$		14,87
8	1-docosene $C_{22}H_{44}$		5,32
9	Tricosane $C_{23}H_{48}$		2,08
10	Tetracosane $C_{24}H_{50}$		4,10
11	Tetracosane $C_{24}H_{50}$		8,20
12	Benzoic acid		3,35

Extract of petroleum-ether

1	Heptadecane $C_{17}H_{36}$		56,84
2	Hexadecane, 7-methyl $C_{17}H_{36}$		3,09
3	1-octadecene $C_{18}H_{36}$		4,06
4	2-Pentad ecanone, 6,10, 14-trimethyl $C_{18}H_{36}O$		8,38
5	5-Eicosene $C_{20}H_{40}$		3,62
6	9-Eicosene $C_{20}H_{40}$		2,29

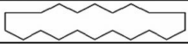
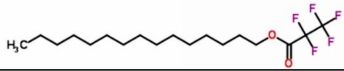
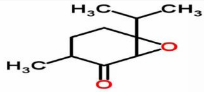
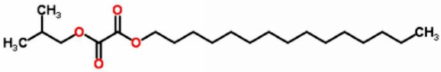
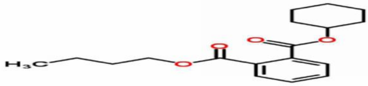
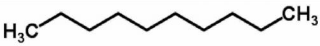
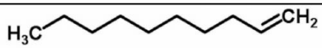
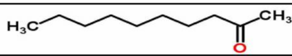
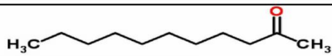
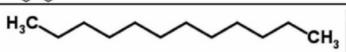
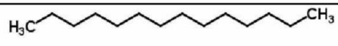
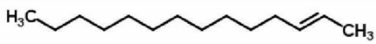
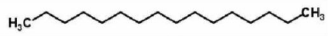
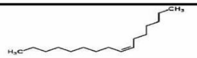
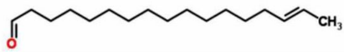
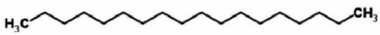
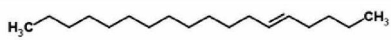
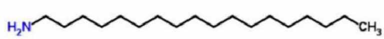
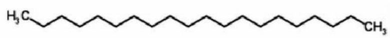
7	Cycloeicosane $C_{20}H_{40}$		2,29
8	Heptafluorobutyryloxyhe-xaadecane		0,71
9	Pentafluoropropionicacid, pentadecylester $C_{18}H_{31}F_5O_2$		0,88
10	7-oxabicyclo [4.1.0] heptan-2-one,6-methyl $C_{10}H_{16}O_2$		1,94
11	Oxalic acid, isobutylpenta-decyl ester $C_{21}H_{40}O_4$		0,97
12	1,2-Benzenedicarboxylic acid, butylcyclohexyl ester $C_{18}H_{24}O_4$		1,77

Table 3b

№	Chemical formula	Structure	%
1	Nonane C_9H_{20}		3,31
2	1-Nonene C_9H_{18}		5,18
3	Decane $C_{10}H_{22}$		3,11
4	1-Decene $C_{10}H_{20}$		4,92
5	2-Decanone $C_{10}H_{20}O$		2,74
6	Undecane $C_{11}H_{24}$		3,15
7	2-Undecanone $C_{11}H_{22}O$		1,99
8	1-Undecene $C_{11}H_{22}$		4,50
9	Cyclododecane $C_{12}H_{24}$		3,22
10	Dodecane $C_{12}H_{26}$		2,69
11	Tridecane $C_{13}H_{28}$		2,78
12	1-Tridecene $C_{13}H_{26}$		2,72

13 Tetradecane $C_{14}H_{30}$		2,45
14 2-Tetradecene, (E)-$C_{14}H_{28}$		3,13
15 Hexadecane $C_{16}H_{34}$		3,30
16 7-Hexadecene, (Z)-$C_{16}H_{32}$		3,03
17 Heptadecane $C_{17}H_{36}$		2,42
18 E-15-Heptadecenal$C_{17}H_{32}O$		2,24
19 Octadecane $C_{18}H_{38}$		2,67
20 5-Octadecene, (E)- $C_{18}H_{36}$		1,79
21 1-Octadecanamine $C_{18}H_{39}N$		2,38
22 Nonadecane $C_{19}H_{40}$		2,72
23 Eicosane $C_{20}H_{42}$		6,57

3.3.1. Lipids from the Biomass (alginates) of mixtures of natural cultures were identical to lipids from the biomass cultivated in laboratory. GLC studies of lipid extracts (methanol-chloroform 1:1) did not show the presence of any paraffin series hydrocarbons. The results of MS studies of oils of both Biomasses (alginates of the Golf and cultivations in Lab) which have undergone pyrolysis did not show the presence of any hydrocarbons. Polysaccharides in microalgae cell wall form a viscous gum like substance by absorbing water molecules (Fig. 5).

3.3.2. Lipids of Sapropel. Results of identification of hydrocarbons by GLC (table 3a) (extracted from methanol) showed that the minimum content (2%) belongs to Tricosane hydrocarbon ($C_{23}H_{48}$) and the maximum (less than 30 %) belongs to Octadecane hydrocarbon ($C_{18}H_{38}$). The extract of Sapropel revealed that almost all of extracted substances (over 91 %) consist of linear, saturated hydrocarbons with C_nH_{2n+2} general formula, where the value of the number n is in the range from 14 to 24.

Only small amounts of derivatives of benzoic acid and unsaturated

1-docosene hydrocarbons ($C_{22}H_{44}$) were identified. The petroleum ether extract of Sapropel showed that Heptadecane - C17H36 content was 57%. Only 25 hydrocarbon compounds have been identified. The list of identified compounds is presented in table 3 a. These hydrocarbons differ from the hydrocarbons extracted from methyl alcohol, by their higher polarities, which are due to the presence of molecules of oxygen and side branching. Also, hydrocarbons of the cyclical and aromatic structures, as well as abundant numbers of linear unsaturated hydrocarbon compounds with C_nH_{2n} formula (where n = 14 to 22) have been found.

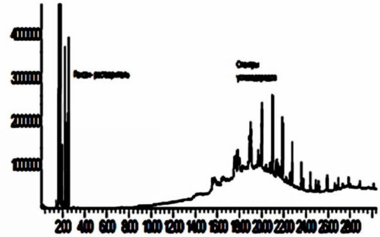
3.3.3. **Pyrolysis oil of Balhashite**. GLC results of the oil have showed the presence of 46 individual compounds. The table 3(b) shows only the hydrocarbons. Their share makes up 73% of the total. They consist of the normal line of saturated and unsaturated hydrocarbons with carbon chain length of C_9 to C_{20}.

Their polar derivatives are formed by bonding of oxygen and nitrogen molecules. More than 35% of total number of hydrocarbons has been found to be the normal saturated hydrocarbons with the CnH2n+2 formulas, where n is the integer from 9 to 20. Unsaturated hydrocarbons of formula C_nH_{2n} (n=9-18) made up about 25% of total numbers of hydrocarbons. All of the unsaturated hydrocarbons contained one double bond. Also, in addition to these hydrocarbons, smaller quantities of polar hydrocarbons were found. Their concentration is more than 9%. Polarity is largely due to the presence of oxygen molecules in the chain, except for 1-Octadecanamin.The polar hydrocarbons are both of saturated and unsaturated nature. It should be noted that fully cyclic structure of cyclododecan hydrocarbons was also present among these hydrocarbons.

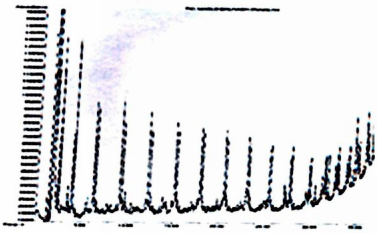
MS data of Balhashite pyrolysis oil showed the presence of about 50 thousand individual compounds.

Most of the individual peaks with high intensity (3,9 %) correspond to about 20 individual components of Balhashite oil (Figure 5) that can be divided into the following groups of lipids:

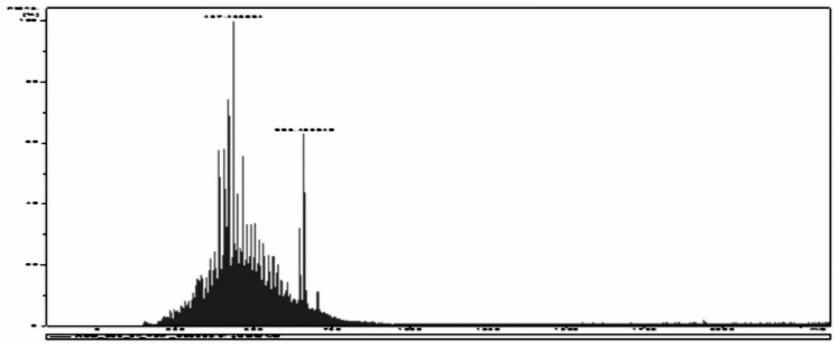
The group of Cerinate hydrocarbons: The maximum peak corresponds to Nonacosanoate $C_{29}H_{57}O_2$ (m/z = 437,4353) which has the structure 



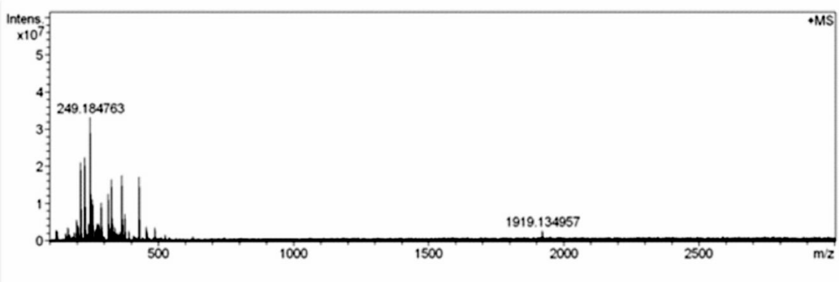
(a)



(b)



(c1)



(c2)

Fig. 5 – GLC data of: a) extracts of Sapropel lipids; b) pyrolysis oil of the Balkhashite; c) MS date of: c1) oil balkhashite; c2) lipids Biomass (alginate)

Moreover, a clear separation of the peaks of this group occur in a strict sequence, starting with Hexacosanoic acid ion (1-), $C_{26}H_{51}O_2$ (m/z=395, 3884) to 2-(2-octyldodecyl) hexadecanoate $C_{36}H_{71}O_2$ (m/z =535, 5449), inclusive.

• A group of Cerotate hydrocarbons (wax) with the distribution range – from Ceryl Cerotate $C_{27}H_{53}O$ (m/z=393, 4091) to Myricyl Cerotate $C_{31}H_{61}O$ (m/z = 449.4717), maximum intensity corresponds to the compound $C_{29}H_{57}O$ (m/z = 421.4404) and alcohols $C_{27}H_{51}O$ (m/z = 391.3934);

• Phosphoric acids of phenyl esters $C_{41}H_{60}O_4$ P (m/z = 647.4224); $C_{42}H_{63}O_4P$ (m/z = 662.4458); $C_{42}H_{64}O_4$ P (m/z = 663.4537).

• Phytosterols (stanols) which are structurally similar to cholesterol; Betasitostanol - $C_{29}H_{55}O$ (m/z = 419.4247); $C_{29}H_{53}O$ (m/z = 417.4091).

Typical net hydrocarbon composition was detected to be 12,3% in oil Balhashite. In addition, there are a long chains alkadienes ($C_{29}H_{56}$, m/z=404,4377; $C_{31}H_{60}$, m/z = 432,4689), alkatrienes (derivatives of fatty acids) in the range of C_{19} ($C_{19}H_{34}$, m/z = 262,2655) C_{41} (C_{41} H_{78}) and botryococcenes (unbranched isoprenoid di-, tri-, tetraterpen hydrocarbons) having the formula of C_nH_{2n-10}. List of detected botryococcenes from pyrolysates of the Balhashite are presented in Table 4. It is also important to note that Tetraterpen hydrocarbons ($C_{40}H_{64}$, m/z=544,5003) and Lycopene $C_{40}H_{56}$, m/z = 536,4377 (a symmetrical tetraterpene assembled from 8 isoprene units) are present in Balhashite oil. Also, MS data detected the presence of squalene (6 isoprene units) $C_{30}H_{50}$ (m/z= 410,3907) and other derivatives representing saturated tetracyclic (sterols) and pentacylic hydrocarbons (hopane - $C_{30}H_{52}$, m/z = 412,4063; lanostane - C30H54 , m/z = 414,422;) The fact that their structures can be built up from isoprene units justifies their classification as terpenes.

4. Discussion of the results

4.1. Microalgae. The chemical composition of the gulf water is fundamentally different from both marine (chloride), and continental (hydrocarbonate) waters. Therefore, it is reasonable to assume that it is this feature of the natural nutrient medium of the gulf, together with other possible abiotic conditions, induces the rapid growth and reproduction of microalgae. As a result, thin layer of film is formed from the mixtures of strains of microalgae on the surface of water. This film is a viscous gum like substance, which is formed by polysaccharides of the microalgae cell wall. In its dry form, the microalgae biomass absorbs water in the amounts preceding its weight by 20-30 times. Absences of hydrocarbons in samples of microalgae biomass that make up the thin film on the water surface indicate that the formation of Balhashite combustible material on water surface is unlikely.

4.2. **Renewable hydrocarbons.** Hydrocarbons of this investigation are classified into 2 types: di-, tri-, tetraterpenoid and nonaterpenoid hydrocarbons derived from fatty acid. The terpenes of Balhashite oil contain both linear and cyclic isoprenoids units (tetracyclic and pentacylic).

Several previously unreported di-, tri- and tetraterpens were defined as botryococcenes in pyrolysate of the Balhashite (table 4).

Table 4

Identification compositions pyloryi's oil of Balchashite by method MS

m/z	I	Molecular formula	% of the total count of pyrolysis oils	примеч.
272,2499	9541333	C 20 H 32	0,082107648	diterpene
284,2499	18028292	C 21 H 32	0,155141913	2n-10
298,2655	18439034	C 22 H 34	0,15867654	2n-10
312,2812	30889600	C 23 H 36	0,265819503	2n-10
326,2968	41062192	C 24 H 38	0,353359431	2n-10
354,3281	34659828	C 26 H 42	0,298264085	2n-10
368,3438	51556928	C 27 H 44	0,443671559	2n-10
382,3594	39041180	C 28 H 46	0,335967675	2n-10
408,3751	53009828	C 30 H 48	0,456174446	triterpene
410,3907	82814960	C 30 H 50	0,712661593	squalene
424,4064	39366436	C 31 H 52	0,338766655	2n-10
438,422	37909716	C 32 H 54	0,326230896	2n-10
452,4377	46004300	C 33 H 56	0,39588859	2n-10
466,4533	42572108	C 34 H 58*	0,366352967	2n-10
480,469	38221728	C 35 H 60	0,328915906	2n-10

494,4846	36836120	C 36 H 62*	0,316992098	2n-10
522,5159	31375510	C 38 H 66	0,270000987	2n-10
550,5472	22364206	C 40 H 70	0,20615214	Tetraterpene
564,5629	22055488	C 41 H 72	0,203306392	2n-10
578,5785	18993214	C 42 H 74	0,175078503	2n-10
620,6255	10807222	C 45 H 80	0,099620435	2n-10
634,6411	11369315	C 46 H 82	0,104801781	2n-10
648,6568	8632937	C 47 H 84	0,079577984	2n-10
662,6724	8926524	C 48 H 86	0,082284255	2n-10

In addition to hydrocarbon paraffin series, lipids samples contain huge amounts of other organic compounds including both hydrocarbons and non-hydrocarbons. Also, there were a lot of oxygen, nitrogen, phosphorus and sulfur containing hydrocarbon derivatives. These characteristics lead to conclusion that obtained hydrocarbons and their derivatives are identical to lipids of algae which can be represented by the general formula $C_1H_{1.83}O_{0.17}\ N_{0.0031}\ P_{0.006}\ S_{0.0014}$. Lipids of microalgae consist of the following main components: Acylglycerides $C_1H_{1.83}\ O_{0.096}$; Glycolipids $C_1H_{1.79}\ O_{0.24}\ S_{0.0035}$; Phospholipids $C_1H_{1.88}\ O_{0.173}\ N_{0.012}\ P_{0.024}$; Algal fatty acid $C_1H_{1.91}\ O_{0.12}$; Methyl esters $C_1H_{1.92}\ O_{0.05}$; Protein $C_1H_{1.56}\ O_{0.3}\ N_{0.26}\ S_{0.006}$; Nucleic acid $C_1H_{1.23}\ O_{0.74}\ N_{0.40}\ P_{0.11}$; Polysaccharide $C_1H_{1.67}\ O_{0.83}$). Renewable hydrocarbons of Lake Balkhash, which have common origin, can be believed to represent the product of Botryococcus balkachicus biosynthesis.

Gatellier et al (2005) and previously revealed that Balhashite combustible material was the result of biosynthesis of race A of Botryococcus braunii. However, the results of this study indicate that these hydrocarbons are not derived from lipids of race A Botryococcus balkachicus. Based on the types of hydrocarbons they synthesize Botryococcus braunii is classified into three principal races (A, B, and L). Race A produces fatty acid derived alkadienes and alkatrienes; race B produces triterpenoids known as botryococcenes and methylsqualenes; and race L produces a tetraterpenoid known as lycopadiene [2]. Bishimbayeva et al (2014) showed that hydrocarbon composition of Botryococcus balkachicus composed of mainly by n-alkanes C21-C38, which constitute 41-62 % of their total number.

Fatty acid composition of intracellular and extracellular lipids is represented by saturated, monounsaturated and diene fatty acids of the C12-C24 length [5]. The results of our study showed that the products of all three races were found in Balhashit. The only difference is that instead of lycopadiene ($C_{40}H_{78}$) our data showed the presence of lycopene ($C_{40}H_{56}$) and phytoene ($C_{40}H_{64}$). For example, lycopene (C_{40}) derivatives are indicative of Botryococcus braunii race L [6,7]. Although reports of the co-existence of different races are rare [8], these data shows the possibility of co-occurrence of 2 or all 3 Botryococcuss balkachicus races in Lake Balkhash. It is most likely reflects the changes in the populations of Botryococcus balkachicus that were caused by the changes in hydrologic conditions.

5. **Conclusion**. These renewable hydrocarbons probably represent products of microalgae lipids from all the three Botryococcus braunii races. Differences in the composition of individual compounds are related to the ratio of the initial strains of microalgae.

The absence of clear morphological differences between the strains of microalgae of Lake Balkhash that produce different types of hydrocarbons: alkenes, botryococcenes (triterpenes) and tetraterpenes (phytoene - $C_{40}H_{64}$ and lycopene – $C_{40}H_{56}$) leads to further study that will focus on identification of the microalgae species. The presence of different unsaturated hydrocarbons is a good renewable source of special chemicals that can be seen as fundamentals of multifunctional technological platforms for the production of many kinds of organic products. Substantial developmental effort is needed to launch large-scale cultivation systems on the Lake Balkhash.

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Donenov Beisen Kainarbayevich, Assoc professor, Director of Association Kazbiofuel, e-mail: beisdonenov@mail.ru, Phone: +7701 425-08-14

Imanbekov Kylysh, Doctor of Chemical Sciences, Assoc professor Head of laboratory: Institute of Chemical Sciences,
e-mail: imanbekov_k.i.2011@mail.ru, Phone: +77077855696, 291-57-70

Kainarbayeva Zhaniya Nurbekovna, Masters candidate,
e-mail: Zhaniya_90nk@mail.ru, Phone: +77474188970

Joldassov Adylbek Musabekovich, Masters candidate,
e-mail: joldassov@gmail.com, Phone: +77760066066

Kozybayev Asylbek, Director of the Research Institute
Food safety, Ph.D., e-mail: asybek_k@mail.ru, Phone: +77772390919