

ENVIRONMENT PROTECTION

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FOR BIOFUEL PRODUCTION IN UKRAINE CONDITIONS**

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E-mail: ¹shamanskiy_s_i@ukr.net; ²chemmotology@ukr.net; ³lenyo@ukr.net**Abstract**

Purpose and Objectives. The article analyses perspectives of the third generation biofuel production out of microalgae biomass in the weather conditions of typical regions of Ukraine. The aim is to model the productivity of biomass and the accumulation of lipids in algae, as well as to calculate the productivity when cultivated in typical regions of Ukraine. **Methods of Research.** By modeling the influence of weather conditions, particularly sunlight irradiation, estimates possibility of achieving crop yields of biomass per square meter of cultivated areas in the weather conditions of typical regions of Ukraine, determines the most perspective regions for it. **Research Results.** The results of calculation of monthly cultivation productivity with respect to microalgae biomass in the five selected regions of Ukraine and results of calculating the annual biomass productivity of cultivation and productivity of accumulated lipids in the same regions of Ukraine are shown. **Discussion.** Microalgae are perspective source of the third and fourth generations for biofuel production. It is possible to achieve crop yields more than 10 kg of biomass per square meter of cultivated areas in the weather conditions of Ukraine. The amount of accumulated lipids in this case can reach 6.6 kg/m². The most perspective regions for cultivation can be considered eastern regions, in particular, the Odesa region. The essential resource, which is necessary for cultivation is water, the basis of the cultural medium. To increase ecological and economic efficiency of cultivation, it proposes using municipal wastewater as cultural medium, combining the cultivation processes and wastewater purification processes from biogenic elements

Keywords: biofuel of the third generation; biogenic elements; eutrophication; microalgae; wastewater**1. Introduction**

There are biofuels of the first, second, third and fourth generations [1-5]. First generation biofuels are produced out of traditional agricultural crops. Food can also be produced out of them. Second generation biofuels are produced out of raw materials that are can not be used for food production. They are different kinds of organic waste. Biofuels of the third generation are produced out of algae. Their advantage is that they do not require fertile areas and can be cultivated in reservoirs, or in tanks located on territories unusable for other purposes. Biofuels of the fourth generation

are also produced out of algae, but out of the species that are able to synthesize hydrocarbons in the process of life activity.

Microalgae are the most productive cultures among aquatic plants. They can be considered as the most promising cultures for the production of biofuels of the third generation. Their cultivation productivity depends on the environmental conditions, such as temperature fluctuations and the presence of sufficient amount of sunlight, which is necessary for the occurrence of photosynthesis. Therefore, average productivity varies in different regions.

2. Analysis of the Research and Publications

Microalgae are effective solar energy converter capable of restoring carbon dioxide to a range of complex energy-intensive molecules such as hydrocarbons, proteins, lipids. This allows them to be used for the further production of biodiesel, bioobutanol, bioethanol, hydrogen, biogas, vitamins, antioxidants, amino acids, etc. [6-9]. Biomass of algae can be successfully used for production of semi-finished products, followed by synthesis of biodegradable polymers out of them. The semi-finished products can include organic acids, such as lactic acid, fumaric acid, succinic acid, malic acid, as paragenic acid, biopolymers.

Different contents of hydrocarbons, proteins and lipids in biomass of microalgae can be obtained by changing conditions of cultivation [10]. To do this, it is necessary to provide optimal cultivation conditions for the selected microalgae culture, such as initial concentration of cells in culture medium, intensity of illumination, temperature, etc. It is possible to cultivate biomass of different biochemical composition by changing these conditions.

There are phototropic, heterotrophic and myxotrophic feeding methods of microalgae. Phototropic method is based on obtaining the required energy by photosynthesis. The source of carbon for phototropic organisms is, basically, carbon dioxide. Heterotrophic method is determined by obtaining energy by consuming organic matter. Mixotrophic method is a combination of the two previous methods. Main characteristics of possible methods of microalgae cultivating are shown in the table 1.

Table 1

Main characteristics of possible methods of microalgae cultivating [11]

Cultivating method	Photo-trophic	Hetero-trophic	Mixo-trophic
Energy source	Light	Organic substances	Light and organic substances
Carbon source	Nonorganic substances (CO ₂)	Organic substances	Nonorganic and Organic substances
Biomass growth rate	Low	High	Medium
Photobioreactor type	Opened or closed	Opened	Closed
Specific cost	Low	Medium	High

To increase the growth rate of phototropic organisms' biomass, heterotrophic and mixotrophic conditions can be applied, since a significant number of microalgae cultures have the properties of adapting to new growth conditions, switching to mixed nutrition methods. Practice shows that the rate of biomass growth of phototropic culture *Chlorella vulgaris* in mixotrophic conditions is 9 to 25 times higher in comparison with phototropic conditions [12].

3. The Aim of Research is to model the productivity of biomass and the accumulation of lipids in algae, as well as to calculate the productivity when cultivated in typical regions of Ukraine.

4. Methods of Research

Intensity of solar radiation at the boundary of the atmosphere is 1367 W/m². When the sky is clear, the surface of the earth receives radiation intensity of 1,000 W/m², the rest is reflected and dissipated by the atmosphere of the planet. When the sky is blocked with clouds solar radiation intensity on the surface of the earth can drop to 50 W/m². The average intensity in many regions of the planet varies from 200 to 250 W/m².

On the territory of Ukraine, the maximum radiation intensity on the earth's surface, subject to cloudless sunny day, may reach 330 W/m² in the summer and 125 W/m² in winter. Zonation of the territory of Ukraine by the average annual intensity of sunlight is shown in figure 1.

Sunlight consists of radiation of different wavelengths. At that, intensity of radiation at different wavelengths is different. Its distribution is shown in figure 2.

Microalgae can use only part of the energy of solar radiation for the processes of photosynthesis. This part of radiation is called photosynthetic active radiation (FAR). It is the driving force of photosynthesis. Wavelengths of FAR lay in in the range from 400 to 700 nm (hatched zone in the fig. 2). This range almost coincides with the range of visible light, which is from 380 to 780 nm.

Intensity of photosynthesis also depends on the wavelength of the absorbed radiation. The dependence of the intensity on the wavelength in the range of FAR is shown in fig. 3.

The FAV range accounts for 45.8% of the total solar energy. It is known that for absorption of one molecule of CO₂ with its consequent transformation into carbohydrates with empirical formula C_m(H₂O)_n

during the photosynthesis, 8 photons are used [14]. Average energy of one photon in the FAR range is estimated as 217.4 kJ. Calorific value of one mole of carbohydrate C(H₂O), and therefore energy stored in it, is estimated as 468 kJ/mol. On this basis, the maximum theoretical efficiency of transformation of FAR energy into hydrocarbons $\epsilon_{FAR \rightarrow C_m(H_2O)_n}$ can be determined by the formula:

$$\epsilon_{FAR \rightarrow C_m(H_2O)_n} = \frac{\epsilon_{C_m(H_2O)_n}}{8 \times \epsilon_{FAR}} \times 100\%, \quad (1)$$

where $\epsilon_{C_m(H_2O)_n}$ – calorific value of one mole of carbohydrate C(H₂O); ϵ_{FAR} – average energy of one photon in the FAR range.

Numerical substitution gives:

$$\epsilon_{FAR \rightarrow C_m(H_2O)_n} = \frac{468}{8 \times 217,4} \times 100\% = 26,9\% . \quad (2)$$

Dissipation and reflection of solar radiation during absorption of solar energy by microalgae organisms lead to additional energy loss. It can be estimated as 10% [17]. Thus, an additional factor of 0.9 can be introduced to take into account dissipation and reflection. Then the maximum theoretical efficiency of absorbing the entire spectrum of solar energy by microalgae organisms during the process of photosynthesis will be

$$\epsilon_{abs} = 0,458 \times 0,269 \times 0,9 \times 100\% = 11,09\% . \quad (3)$$

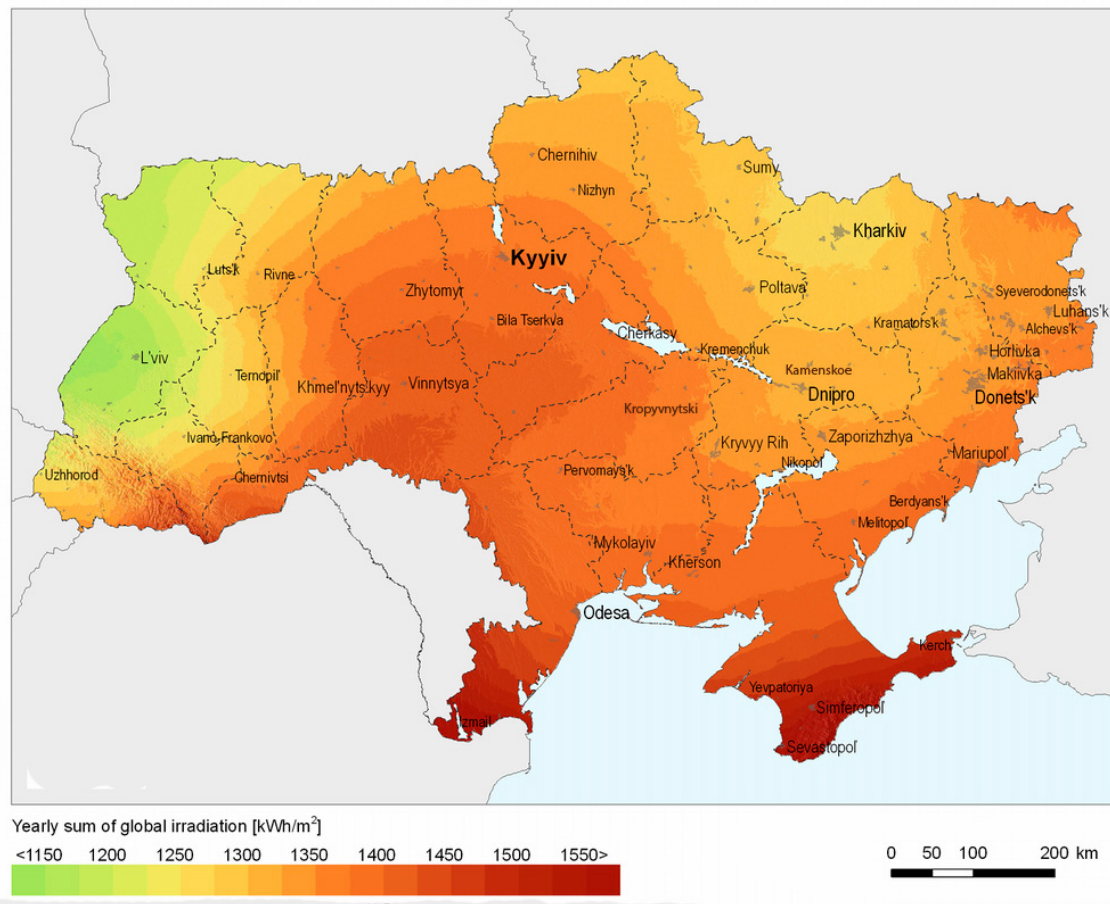


Fig. 1. Zoning of the territory of Ukraine according to sunlight intensity [14]

Such a model does not reflect well the reality. Studies show that in real conditions, the efficiency of solar energy absorption during photosynthesis is much lower and can be estimated as 3-6% [17]. It occurs because of additional energy losses due to

photo inhibition, night breathing of photosynthetic organisms etc.

To simulate the influence solar light intensity on the productivity of microalgae cultivating, it is possible to use the energy balance of photosynthesis [18].

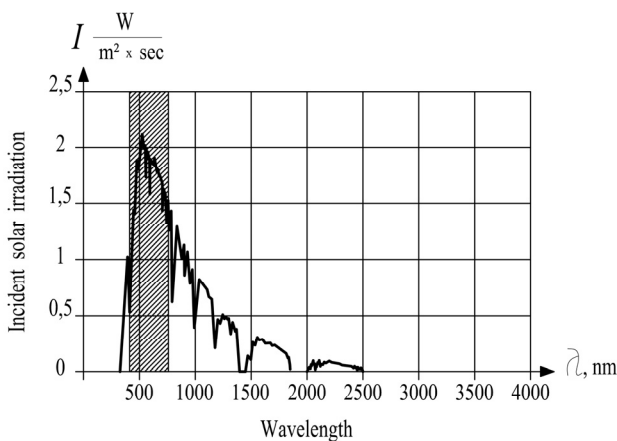


Fig. 2. Intensity of solar radiation at different wavelengths [15]

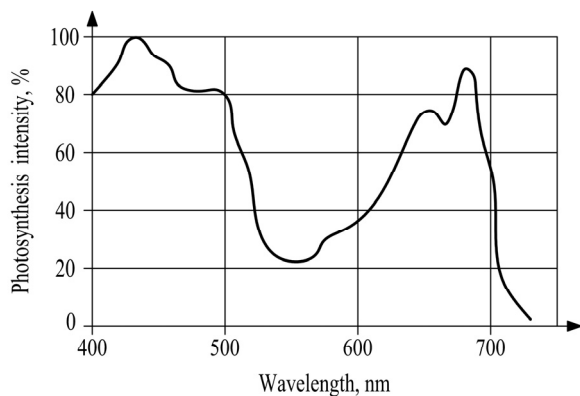


Fig. 3. Dependence of photosynthesis intensity on wavelength in the FAR range [16]

Let's consider the influence of the culture medium illumination on daily amount of biomass, obtained from the unit of photobio-reactor area Π_{biom} . It can be determined by the formula

$$\Pi_{biom} = \frac{I_{illum}}{E_{biom}} \times k_{transf} \times k_{conv}, \quad (\text{g/m}^2 \cdot \text{day}), \quad (4)$$

where I_{illum} – solar energy, falling per unit of photobioreactors area ($\text{kJ/m}^2 \cdot \text{day}$);

E_{biom} – amount of energy, stored in one kilogram of microalgae biomass (MJ/kg);

k_{transf} – efficiency coefficient of transfer of solar energy to microalgae organisms;

k_{conv} – efficiency coefficient of conversion of received solar energy into biomass by microalgae organisms.

Efficiency coefficient of transfer of solar energy to microalgae organisms can be determined by the formula

$$k_{transf} = k_{prop} \times k_{area} \times k_{PAR} \times k_{abs}, \quad (5)$$

where k_{prop} – efficiency coefficient of solar light propagation through culture medium with microalgae (takes into account dissipation of solar radiation in the environment);

k_{area} – efficiency coefficient of using photobioreactors illuminated area (quantitatively equal to the ratio of the illuminated surface of the culture medium to the entire illuminated surface of the reactor);

k_{PAR} – coefficient of photosynthetic active solar radiation;

k_{abs} – coefficient of solar energy absorption by organisms of microalgae.

Efficiency coefficient of conversion of received solar energy into biomass by microalgae organisms can be determined by the formula

$$k_{conv} = k_{photon.abs} \times k_{photon.fix} \times (1 - k_{breath}), \quad (6)$$

where $k_{photon.abs}$ – coefficient of photon absorption efficiency during photosynthesis;

$k_{photon.fix}$ – coefficient of fixation efficiency of absorbed photons energy during photosynthesis;

k_{breath} – coefficient of energy loss due to night breathing by microalgae organisms.

Under optimum conditions, microalgae must absorb all the sunlight photons that reach them. Since the actual conditions of cultivation are not optimal, for example, the level of illumination may be too high, the temperature may differ from the optimum value, etc. In this case, the phenomenon of photo inhibition can occur and the value of the coefficient of fixation efficiency $k_{photon.fix}$ decreases.

At high temperatures of the medium, sunlight photons, absorbed by the cells of microalgae, can be emitted back into the environment in the form of thermal radiation. If the illumination of microalgae is too high, photons can damaged their cells.

The level of illumination, at which the highest intensity of photosynthesis is achieved, is called saturation level. For most microalgae cultures saturation is observed at a photon flux density of $200 \mu\text{mol/m}^2 \cdot \text{sec}$ [19].

In general, at low values of illumination, with its growth, the intensity of photosynthesis increases in direct proportion. For higher values of illumination, there is an increase in logarithmic proportion. If the illumination increases over saturation level, the intensity of photosynthesis decreases (for significant number of microalgae cultures).

Coefficient of fixation efficiency of absorbed photons energy during photosynthesis can be determined by the formula

$$k_{\text{photon.fix}} = \frac{I_{\text{sat}}}{I_{\text{inc}}} \times \left[\ln \left(\frac{I_{\text{inc}}}{I_{\text{sat}}} \right) + 1 \right], \quad (7)$$

where I_{sat} – saturation density sunlight ($\mu\text{mol}/\text{m}^2 \cdot \text{sec}$);

I_{inc} – incident sunlight density ($\mu\text{mol}/\text{m}^2 \cdot \text{sec}$).

Dependence of the coefficient of fixation efficiency $k_{\text{photon.fix}}$ on the ratio $I_{\text{inc}}/I_{\text{sat}}$ is logarithmic (see formula 7). Graphically, this dependence is shown in figure 4, where linear coordinates are used.

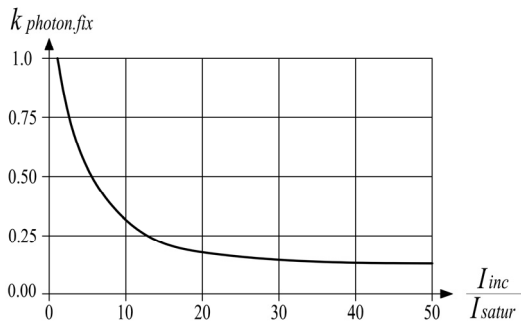


Fig. 4. Dependence the coefficient of fixation efficiency of absorbed photons energy during photosynthesis the ratio of incident sunlight density to saturation density

Figure 4 the coefficient of fixation efficiency $k_{\text{photon.fix}} = 1$ for the ratio $I_{\text{inc}}/I_{\text{sat}} = 1$ and decreases with this increasing ratio. In accordance with formula 7, when the ratio $I_{\text{inc}}/I_{\text{sat}} < 1$, coefficient $k_{\text{photon.fix}}$ is sharply decreasing with ratio decreasing. This does not match the experimental data. At low incident sunlight density, value of $k_{\text{photon.fix}}$ remains close to one. Because of this, formula 7 can be used only in the range $I_{\text{inc}}/I_{\text{sat}} \geq 1$.

Daily amount of lipids, accumulated in the biomass of microalgae, cultivated per unit area of photobioreactor can be determined by the formula

$$\Pi_{\text{lip}} = \frac{k_{\text{lip}} \times \Pi_{\text{biom}}}{\rho_{\text{lip}}} \quad (\text{ml}/\text{m}^2 \cdot \text{day}), \quad (8)$$

where k_{lip} – coefficient of lipid content in microalgae biomass;

ρ_{lip} – density of lipids, accumulated in the biomass (kg/l).

5. Research Results

Averaged data of observations of solar radiation density on the territory of Ukraine, carried out by NASA during 20 years are shown in table 2. The data reflect average monthly density of solar radiation in the main (typical) regions of Ukraine.

Table 2

The average monthly density of solar radiation in the main (typical) regions of Ukraine, kWh/m²·day [14]

Region	Months											
	01	02	03	04	05	06	07	08	09	10	11	12
Kyiv	1,07	1,87	2,95	3,96	5,25	5,22	5,25	4,67	3,12	1,94	1,02	0,86
Lviv	1,08	1,83	2,82	3,78	4,67	4,83	4,83	4,45	3,00	1,85	1,06	0,83
Poltava	1,18	1,96	3,05	4,00	5,40	5,44	5,51	4,87	3,42	2,11	1,15	0,91
Dnipro	1,21	1,99	2,98	4,05	5,55	5,57	5,70	5,08	3,66	2,27	1,20	0,96
Odesa	1,25	2,11	3,08	4,38	5,65	5,85	6,04	5,33	3,93	2,52	1,36	1,04

Let's calculate monthly and annual productivity of microalgae cultivation with respect to its biomass and accumulated lipids in the weather conditions of the main regions of Ukraine. Biomass productivity

can be determined by the formula 4, accumulated lipids productivity – by the formula 8.

Energy amount, stored in the biomass unit of cultivated microalgae was taken $E_{\text{biom}} = 30.0 \text{ MJ/kg}$ [20, 21].

To calculate the efficiency coefficient of transfer of solar energy to microalgae organisms k_{transf} by the formula (5) the next values of included coefficients were taken: $k_{prop} = 0,98$, $k_{area} = 0,98$ as for open capacities [17], $k_{PAR} = 0,458$ [22], $k_{abs} = 1,0$ [18].

To calculate efficiency coefficient of conversion of received solar energy into biomass k_{conv} by the formula 6, coefficient of photon absorption efficiency during photosynthesis was taken $k_{photon.abs} = 0.269$ (see calculation of theoretical efficiency of transformation FAR energy into hydrocarbons $\mathcal{E}_{FAR \rightarrow C_m(H_2O)_n}$, formula 1). Coefficient of energy loss due to night breathing was taken $k_{breath} = 0.2$ [18].

To calculate the coefficient of fixation efficiency of absorbed photons energy $k_{photon.fix}$ by the formula (7), saturation density sunlight was taken $I_{satur} = 200 \mu\text{mol}/\text{m}^2 \cdot \text{sec}$. As the density of incident light I_{inc} the average monthly density of solar radiation was taken according to NASA (see table

2). The density was expressed in $\mu\text{mol}/\text{m}^2 \cdot \text{sec}$ previously. For the months for which the condition $I_{inc}/I_{satur} \geq 1$ is not met, coefficient of fixation efficiency was taken $k_{photon.fix} = 0,99$.

Daily amount of lipids, accumulated in the biomass of microalgae by the formula (8), the coefficient of lipid content in microalgae biomass was taken $k_{lip} = 0,2$, which, according to [21, 23-25], is one of the lowest possible. Density of lipids, accumulated in the biomass, was taken $\rho_{lip} = 0.85 \text{ kg}/\text{liter}$ [26].

The results of calculation of monthly cultivation productivity with respect to microalgae biomass in the five selected regions of Ukraine are shown in figure 5. The results of calculating the annual biomass productivity of cultivation and productivity of accumulated lipids in the same regions of Ukraine are shown in figure 6.

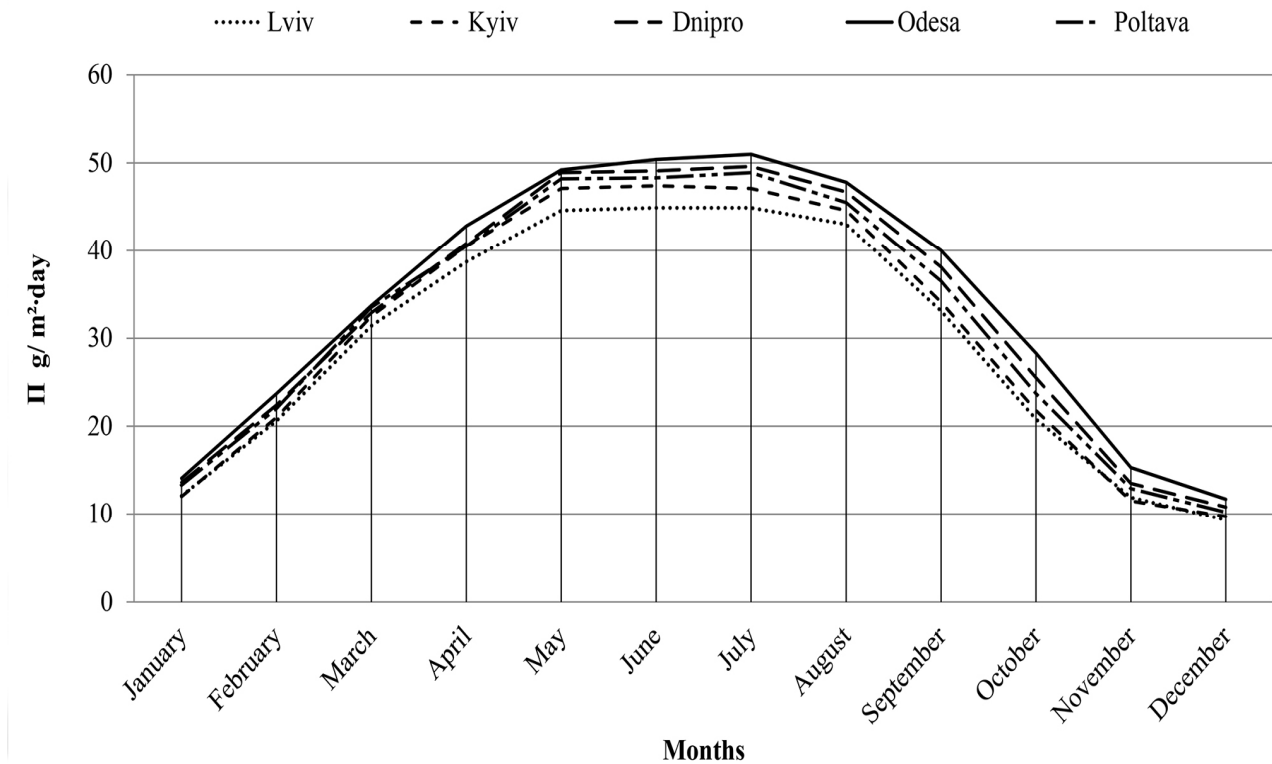


Fig. 5. Monthly biomass productivity of microalgae cultivation in typical regions of Ukraine, kg/m^2

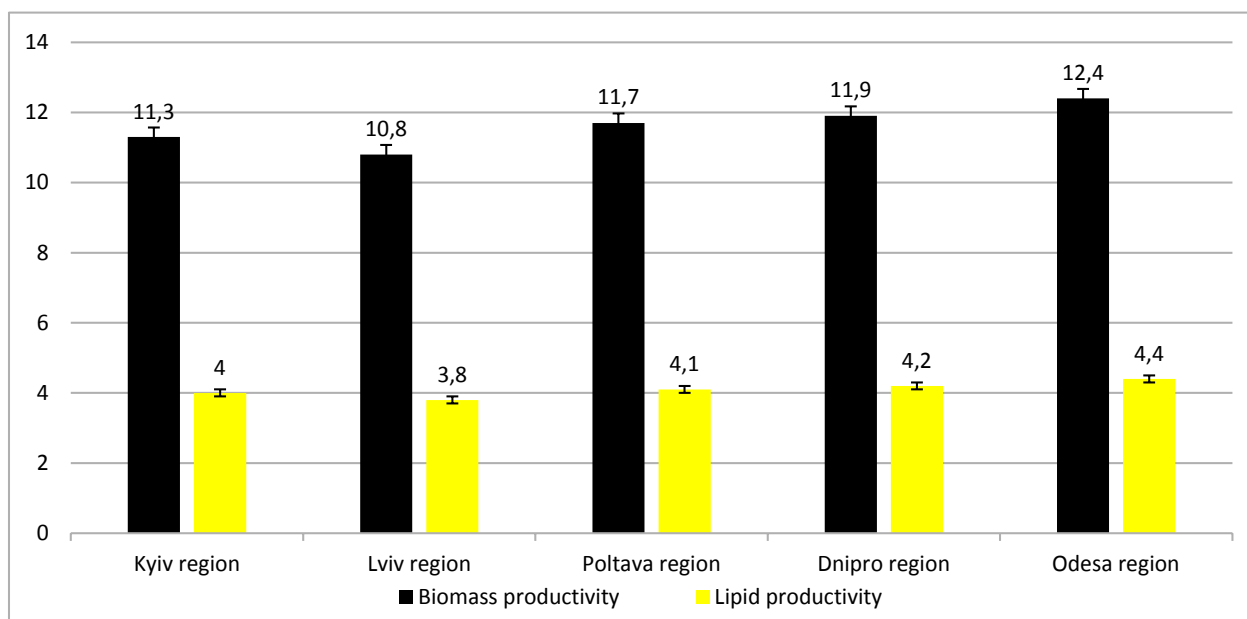


Fig. 6. Annual biomass and lipid productivity of microalgae cultivation in typical regions of Ukraine, kg/m²

6. Discussion

Microalgae cultivation requires significant amount of energy. Taking into account that Ukraine's weather conditions are not among the most favorable in comparison with other regions of the world, the cost of cultivation in Ukraine is expected to be high [27]. To carry out the process of photosynthesis microalgae require biogenic elements. They must be added to the culture medium [28-30]. To reduce the cost of cultivation and provide its higher ecological and economic efficiency, it is proposed to use mechanically purified municipal wastewater as cultural medium [31-33]. The wastewater can contain significant amount of nutrients, especially nitrogen and phosphorus compounds. Household wastewater can contain total phosphorus from 5 to 20 g/m³ [34]. Phosphorus contribution of one inhabitant of residential area to residential sewerage is estimated from 0.65 to 4.80 g/day. The average value is 2.18 g/day. This contribution tends to increase due to constantly increasing usage of detergents. Household wastewater can also contain total nitrogen from 50 to 60 g/m³ [35]. The amount can vary depending on the origin of wastewater.

Traditional sewage treatment plants with biological treatment have efficiency of phosphorus removal from wastewater about 20%. When the plants apply technology, which does not use denitrification process, they have efficiency of nitrogen removal from wastewater from 20 to 35%.

That means that residual concentration of nitrogen and phosphorous in purified wastewater is significant even after biological treatment. Discharging this wastewater into open waterbodies is often the cause of their eutrophication (intensive development of phytoplankton, especially on the surface of waterbodies). This phytoplankton prevents sunlight and oxygen penetration of into the water depth, which leads to death of flora and fauna. It is known that a gram of phosphate compounds in open waterbody, if other conditions are favorable, causes blue-green algae biomass growth from 5 to 10 kg. After treatment of municipal wastewater with microalgae can help to reduce the risks of eutrophication processes development and increase the level of environmental safety.

7. Conclusions

Microalgae are perspective source of the third and fourth generations for biofuel production. It is possible to achieve crop yields more than 10 kg of biomass per square meter of cultivated areas in the weather conditions of Ukraine. The amount of accumulated lipids in this case can reach 6.6 kg/m². The most perspective regions for cultivation can be considered eastern regions, in particular, the Odesa region. The essential resource, which is necessary for cultivation is water. It is the basis of the cultural medium. To increase ecological and economic efficiency of cultivation, municipal wastewater can be used as cultural medium. It is possible to combine

the processes of cultivation and processes of wastewater purification from biogenic elements (nitrogen and phosphorous compounds). Experience shows that when using wastewater as culture medium, using fresh water can be reduced up to 90%. Wastewater treatment with microalgae can help to reduce discharges of biogenic elements in surface water bodies, thus reducing their potential for eutrophication. It is also allows obtaining additional renewable energy sources, primarily in the form of biodiesel, made from microalgae biomass.

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Оцінювання продуктивності культивування мікрводоростей для виробництва біопалива в умовах України

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Мета та задачі. У статті аналізуються перспективи виробництва біопалива третього покоління з біомаси мікрводоростей у погодних умовах типових регіонів України. Метою є моделювання продуктивності біомаси та накопичення ліпідів у водоростях, а також для підрахунку продуктивності при вирощуванні в типових регіонах України. **Методи дослідження.** Моделюючи вплив погодних умов, особливо сонячного випромінювання, оцінюється можливість досягнення врожайності біомаси на квадратний метр оброблюваних площ у погодних умовах типових регіонів України, визначаючи

для неї найбільш перспективні регіони. **Результати досліджень.** Показані результати розрахунку щомісячної продуктивності вирощування щодо біомаси мікродоростей у п'яти обраних регіонах України та результати розрахунку річної продуктивності біомаси вирощування та продуктивності накопичених ліпідів у тих же регіонах України. **Обговорення.** Мікродорості є перспективним джерелом виробництва біопалива третього та четвертого покоління. В погодних умовах України можна досягти врожайності понад 10 кг біомаси на квадратний метр оброблених площ. Кількість накопичених ліпідів у цьому випадку може досягати 6,6 кг/м². Найбільш перспективні регіони для вирощування можна вважати східними регіонами, зокрема, Одесою. Основним ресурсом, який необхідний для обробітку, є вода, основа культурного середовища. Для підвищення екологічної та економічної ефективності вирощування пропонується використовувати муніципальні стічні води як культурне середовище, поєднуючи процеси вирощування та очищення стічних вод від біогенних елементів.

Ключові слова: біогенні елементи; біопаливо третього покоління; евтрофікація; мікродорості; стічні води.

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Оценка производительности культивирования микродорослей для производства биотоплива в условиях Украины

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Цель и задачи. В статье анализируются перспективы производства биотоплива третьего поколения из биомассы микродорослей в погодных условиях типичных регионов Украины. Цель состоит в том, чтобы моделировать продуктивность биомассы и накопление липидов в водорослях, а также рассчитывать производительность при выращивании в типичных регионах Украины. **Методы исследования.** При моделировании влияния погодных условий, в частности облучения солнечным светом, оценка возможности получения урожайности биомассы на квадратный метр культивируемых площадей в погодных условиях типичных регионов Украины определяет наиболее перспективные для нее регионы. **Результаты исследований.** Показаны результаты расчета ежемесячной продуктивности выращивания в отношении биомассы микродорослей в пяти отобранных регионах Украины и результаты расчета годовой урожайности биомассы выращивания и продуктивности накопленных липидов в тех же регионах Украины. **Обсуждение.** Микродоросли являются перспективным источником производства биотоплива третьего и четвертого поколений. В погодных условиях Украины можно достичь урожайности более 10 кг биомассы на квадратный метр культурных площадей. Количество накопленных липидов в этом случае может достигать 6,6 кг/м². Наиболее перспективными регионами для выращивания можно считать восточные регионы, в частности Одесскую область. Основным ресурсом, который необходим для выращивания, является вода, основа культурной среды. Для повышения экологической и экономической эффективности культивирования предлагается использовать муниципальные сточные воды в качестве культурной среды, сочетая процессы культивации и очистки сточных вод от биогенных элементов.

Ключевые слова: биогенные элементы; биотопливо третьего поколения; микродоросли; сточные воды; евтрофикация.

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