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MICROALGAE PRODUCTION IN SERVICE OF FUEL PRODUCTION

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Driven by the rising need for biofuels because of the constant rise in the world market price of crude oil, and by the necessity to capture carbon dioxide, autotroph organisms got into the spotlight of energetic research. Algae production is the most promising solution amongst the alternatives because of its specific area necessity and high reproduction rate. Research on the whole range of algae cultivation and processing is done at the Department of Chemical Engineering of the University of Pannonia. The utilization of algacultures in experimental photobioreactors is examined, together with the optimization of the operational conditions both for artificial and natural light and with different fertilizers. The various parameters of alga-processing is also determined. Based on literature data and experiments conducted in Veszprém, in this paper we give an overview of the planning, operation and processing principles connected to algae reactors.

Keywords: algae, oilgae, algae photobioreactor

Introduction

Carbon-dioxide emission volume is one of the highest of air pollutants in the world. Carbon capture and storage needs rise year by year. There are spoantaneous environmental procedures to feed CO_2. Using these procedures we can feed back the carbon content of CO_2 into biological systems and we can get a number of valuable organic compounds, among others biofuel, to reach ecological and economical benefits.

Algae research is not as novel as it seems at first. Algae growing began in about the first quarter of last century. Scientist thought the food source of the future could be green algae farms. Although the vision falls by insufficient sponsorship, but most of general rules of growing was discovered. Algae based fuel technology first mentioned in the beginning of the 1950's. Some pilot plant to grow algae as energy source was built in 1970's. Algae oil production for fuel technology first mentioned in the 1980's and lives its renessaince 21st century [1, 2].

Autotrophic organisms as energy sources

Autotrophic organisms synthetizes complicated organic compunds which need them to build up their own cells. These organisms can be monocytae (microalgae) or other differentiated autotrophics (e.g. corn, soy beans). The needs of these photosynthetizing creatures can generally be categorized in five groups.

In the first group there are the environmental parameters. Light has a special function since it supplies the energetic background of the biochemical reactions in the light period

The second gruoup is the concentration of CO_2 and its derivatives in aquenous solution. These contents supply the great majority of carbon content of the photosynthetics cell. We use CO_2 as a fetilizer to reach higher biomass productivity [3].

The third group is primary macronutrients (NPK). Nitrogen (N) is a major component of proteins, hormones, chlorophyll, vitamins and enzymes essential for plant life. Phosphorus (P) is necessary for photosynthesis, protein formation and almost all aspects of growth and metabolism. Potassium (K) is necessary for the formation of sugars, starches, carbohydrates, for protein synthesis and cell division in plants.

The fourth group is primary macronutrients (Ca, S, Mg). Sulfur (S) is a structural component of amino acids, proteins, vitamins and enzymes and is essential to produce chlorophyll. Magnesium (Mg) is a critical structural component of the chlorophyll molecule and is necessary for functioning of plant enzymes to produce carbohydrates, sugars and fats. Calcium (Ca) plays a role in the functioning of enzymes, is part of the structure of cell walls, helps control the water content of cells, and is necessary for cell growth and division.

The fifth group is micronutrients or trace minerals. Iron (Fe) is necessary for enzyme functionality and is important for the synthesis of chlorophyll. Manganese (Mn) is involved in enzyme activity for photosynthesis, respiration, and nitrogen metabolism. Boron (B) is used in cell wall formation, for membrane integrity within cells, for calcium uptake and may aid in the transfer of nutritional sugars between plant parts. Zinc (Zn) is a component of enzymes or as an important aid in the functioning of them. Copper (Cu) takes part in nitrogen metabolism. Molybdenum (Mo) is a structural component of the enzyme that reduces nitrates to ammonia. Without it, the synthesis of proteins is blocked. Nickel (Ni) is required for iron absorption. Cobalt (Co) is required for nitrogen fixation, so a deficiency could result in nitrogen deficiency symptoms. Sodium (Na) and chlorine (Cl) are involved in the osmotic (water movement) and ionic balance in plants (much as is people).

There is the annual oil productivity specification of autotrophic organisms in *Table 1.* These organisms are potentially used for oil production. The microalgae oil productivity in prosperous circumstances is at least 8 times higher than others.

Table 1: Oil productivity of autotrophic organisms

Organism	*Oil, liters/hectare/year*
Soya	440
Sunflower	900
Rapeseed	1 150
Palmoil	5 400
Microalgae	40 000–135 000

Nowadays algae growing is in limelight due to its high productivity. Additional benefits are that there is no need to use growing fields and some wastewater may be used with nutrient supplementation.

Algae species for oil production

Algae are a large goup of simple, typically autotrophic organisms. They are eucaryotic, autotrophic, unicellular or multicellular form. Their size can change wide range (micrometers to meters). Algae have nuclei enclosed in membrane and plastids bound in one or more membranes. There are chloroplastics in the cell, which contain bioactive compounds for photosynthesis. These compounds function is transferring the energy of light to biochemical reactions. Hereinafter parameters are about freshwater algae, but some observations might be applicable to seawater species.

Algae species are applicable for energetic purposes wich produce lipids as more as it possible in their whole growing period. Some of these species' lypide content may be more than 40 percent of their own weight. These lypides mostly contents glycerine esthers of various C_{16}-C_{20} fatty acides. These compounds are applicable for biodiesel production. [4]

Table 2 shows the organic composition of some algae.

It is important that these parameters are only valid at properly equal conditions of the source. In case of changing culturing, environmental and other parameters productivity may shows such enormous difference. It is important to notice that high lipid content does not necessarily mean a high biomass growing potential. [6, 7, 8, 9, 10, 11].

Table 2: Common alga species used for energy biomass and energy production (contents in wt.%) [5]

Microalga	*Protein*	*Carbo-hydrate*	*Lypides*
Primnesium parvum	28–45	25–33	22–38
Scenedesmus dimorphus	8–18	21–52	16–40
Chlorella vulgaris	51–58	12–17	14–22
Dunaliella bioculata	49	4	8
Euglena gracilis	39–61	14–18	14–20
Spirulina maxima	60–71	13–16	6–7

Circumstances of growing

Algae get nutrients and other compounds from aqueous solution. On one hand they consume inorganic compounds and simple organic compounds, on the other hand they feed CO_2 in the form of hydrogencarbonate from dissolved gas mixture. Choosing the right growing conditions has a positive effect on the whole process. Continous measuring of all parameters are not necessary. A proper routine for the analytics can give as enough information as we need. For example a photometric test can give information about population and partially about the composition of the cells.

Environmetal parameters

Where environmental parameters are same at the major part of the year growing is so easier to manage than continental areas where weather is more complicated. We should keep on eye on weather forecast to plan procedures and the whole supply chain.

Available light is an essentially limiting factor for photosynthetic organisms. At natural conditions numerous alga species can live together in the same medium. In these media each species have competitive advantage beacause of the change of daylight spectra and intensity. The diversity of species remains because the light parameters change in every part of the day.

Green algae produce biomass by photoautotrophic production. In this method absorbed solar energy is transformed to chemical energy. For further energetic inspection this process can be drawn as given below (the nitrogen source is ammonia):

$$1\ CO_2 + x\ NH_3 + y\ H_2O \rightarrow 1\ CH_{1,78}O_{0,36}N_{0,12}$$

Theoretically at least 14 moles of photones is necessary to build 1 mole of CO_2 for biomass production. This rate is the same for microalgae too. Assimilating 1 mol of CO_2 produces 1 mol of biomass. Its molar mass is about 21.25 g/mol and its heat of combustion is 547.8 kJ/mol (25.8 kJ/g biomass).

Autotrophic organisms use only a part of total sunlight spectrum (400–700 nm) for photosynthesis. This range is 42.3 % of the total spectrum. This is called *photosynthetic active radiation* (PAR). The average energy of the photones is 218 kJ/mol in this interval. The maximum theoretical photosynthetic energy efficience (PE) can be determined from these data given above. PE is 9 % for the total spectrum of sunligh and it is 21.4 % for the range of PAR.

Another environmental parameter is the ambient temperature and its effect on the reactor. Warming up of a dense algae suspension without cooling can reach much higher temperature than ambient temperature. Increasing suspension density causes increasing heat absorbtion from sunlight. Algae optimally proliferate between 20–40 °C. Below this range their metabolism is slowed down. Above this range their decomposition by heat shock is rising with the rise of the temperature.

Fertilizing with CO_2

CO_2 feed means that the bubbling of a gas mixture into the algae suspension. Generally, this mixture contains about 5–30 vol% CO_2 and air is the rest. It is possible to grow algae in gas mixtures without air, but their oxygen content for the dark period is an essence. The applicable CO_2 concentration depends on the temperature and liquid fertilizer concentration too. Althogh the liquid concentration of CO_2 decreases by the rise of temperature but solved gas is used higher efficiency by the rise of metabolism than at lower temperature. In case toxic components are in the CO_2 source (eg. SO_x, NO_x), then air mixing might be essential. The air supply must be free of dust, mineral oil and other harmful particles (e. g. Microbes).

The medium

There are significant differences in nutrient requirement among species of the same alga genus. Accordingly, an optimal nutrient composition for a specified alga might not be applicable for another species in the same genus. Commonly an optimized medium composition is only valid and applicable in the same circumstances as observed. It is an important to mention that in these systems single nutrient composition changes do not have effets of the same intensity than in combination with another nutrient(s). There are multilateral effects between nutient component concentrations, these connections might be a relevant information.

There are a lot of media recipes accessible. There are recommendations for the most algae species. Athough media for smaller volumes are more complicated than media used for higher volumes of algae suspension. An important point is to use some kind of comlplex formula to keep micronutrients accesible for algae.

Photobioreactors

We use special photobioreactors to keep specified cultivation parameters. Common expectations are specified below.

It is important that as much PAR type light as possible be accesible for the algae. Input and output streams must be safeand well measured for CO_2 content of the gas mixture. These reactors must be designed to resist environmental effects (wind, rain, sunlight, insects etc.). These algae suspensions must be well stirred, because degradation might be started in subsided algae conglomerate.

These reactors must be designed for local microclimate and mostly mounted with cooling system. The planned cultivating volume affects the reactor geometry.

The largest volume can be reached in open pond systems. In this case we can keep those type of algae which are resistant against local microbes and environmetal effects. To avoid invasive species proliferation parameters must be well monitored. Generally, mechanical stirring is applied to maintain aeriation and stirring.

Another open type cultivation is the raceway system. In this case algae suspension flows in a canal. The thickness of the layer is between 100–500 mm.

Another type of cultivation can be in closed photobioreactors. These reactors have a well-defined area of light trasmitting wall. This is critical to the design. We should reckon with shadows of statically necessary elements on the light side. Inner or outer contaminations of walls must be regularly eliminated. Source of outer contaminations origin can be technical (e. g. scratches) or other environmental (e. g. dust). Important is the choice of optimal thickness of layer to reach sufficient mixing. A thoughtful reactor design and monitored inputs can assure a well balanced algae cultivating system with low risk of unwanted external effects.

Closed photobioreactors are built in two designs. The first is the pipe system, with the advantages of simple geometry and few shading element but it has the disadvantage of low area by volumetric unit. The second type is the panel with the advantage of high area of volumetric unit and the disadvantage of evolving idle spaces.

The harvest

Harvest is a critical phase of the technology. This is the limit between the active and inactive phase of algae. Its time must be determined by the quality of the algae suspension. To choose the appropriate date, we should know the algae’s behaviour at the current parameters.

Following biologists instructions in case of ideal parameters an algae culture goes through four main growth phases.

The first is getting acclimatized. It can lasts from a few hours to 1-2 days. It is probably affected by the change of environmental parameters. The second is the quick growth or exponentional phase when significant biomass multiplication is shown. In this phase batch harvesting is too early. After this, a maximum is reached in biomass concentration. The next phase is the decrease of biomass comcentration. In this phase algae should be harvested. At the end of this phase there are a few algae in population and the chances are that other harmful microorganisms have been proliferated.

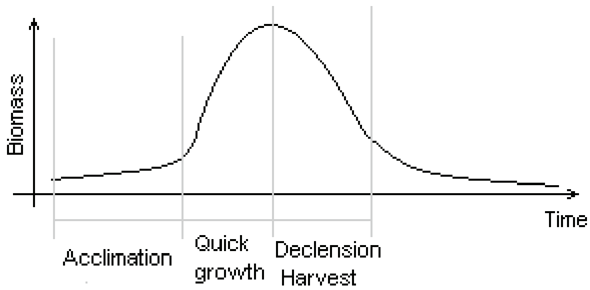

Figure 1: Population vs. age of population

We can choose from two opposite harvesting strategies. One of them is the batch type when total harvest and refill periods follow each other. In this case we use a new sterile starter culture. Its advantage is that the previous batch does not affect to the next but its disadvantage is the need of a separate infrastructure to supply eligible quality and quantity starter culture. The other leads to quasi-continious systems. In this case part of the culture is harvested and restored with fresh medium. Its advantage is the ability of simple automation system but the disatvantage is the need of a proper harvesting schedule. It is important to avoid the proliferation of harmful microbes and important to monitor the accumulation of metabolites.

Concentrating algae suspension, oil extraction (13-18)

Algal oil extraction consists of 2 necessary steps. One of them is the concentration of the alga biomass and the other is the lipid extraction. Lots of techniques are applicable for this purpose. The most common types of techniques and their tipical examples are summarized below. If any of these is to be chosen it is important to consider that we should get the most biocomponent by using the least energy consumption as possible.

Concentrating the algae suspension

Although settling has the least energy consumption of concentration but mostly the rest of dry content cannot be precipitated. In this case some kind of pre-treating is necessary. Flocculation is a widely applicated technology in wastewater treatment technologies. Cationic poly-electrolytes are used for algae flocculation. After addition of these polyelectrolytes settling and filtering of evolved flocks becomes easier. It is important to notice that the use of polyelectrolytes may affect the oil extraction. In case of insufficient flocculation centrifugation is also used but it is important to reconsider since it means investing more energy.

At the end of the concentrating phase we get a biomass with a low moisture content. It is important to know that this material should be processed as soon as possible. It can be stored after drying in inert atmosphere or frozen.

Algal oil extraction

Algal oil extraction can be carried out in two startegies. One of them is to extract oil from dry or moist material. The other is cell degradation come before extraction. The latter can be made by ultrasonic, microwave radiation, chilling shock, cell blast, enzymatic process. The aim of these methods that let intracellular compounds achievable for extracting material.

In *Table 3* we present some common used solvent systems. In complex solvent systems, the polarity order is kept.

Table 3: Common solvent systems for algae extraction

Extraction	*Solvent1*	*Solvent2*	*Solvent3*
Solid-liquid	Chloroform	Methanol	Water
	Hexane	I-Propanol	Water
	Hexane	Ethanol	Water
	Ethanol	1- buthanol	Water
	Acetone	hexane	
Superchritical fluid	CO_2, Water, methanol, buthane, penthane		
Novel techniques	Ultrasonic, Microwave, ASE, Cell-milking, Liquid dimethyl-ether		

Use of supercritical extraction is not so competitive but there are researches to get the optimal fluid-cosolvent pair.

There are more and more new algal oil extraction can be reached. Some of these keeps to solvent free technologies [19] others lead to new solvent base ones. [20, 21, 22].

Algae technology research at the University of Pannonia

Research in algae cultivation and algal oil extraction is carried out at the Department of Chemical Engineering at the University of Pannonia. Together with industrial partners, we deal with the selection and testing of lipids, other bioactive compounds and alga species capable of biomass production. We also deal with the examination of optimal operational conditions of photobioreactors and the development of algae processing technologies. The available photobioreactors make the examination of different alga species with natural and artificial illumnation and with the intake of gas mixtures of different composition possible.

Conclusion

Cultivation and processing of algae for fuel production is a promising research area because of the potentially high yield. However, most of the present technological solutions require development. The most important goal is to get the best yield with the lowest investment of materials and energy. A possible experimental path which has not been described in detail above is GMO, the introduction of which to industrial production has possible benefits, but also needs caution in order to prevent the natural ecosystem.

The other important question – as for all novel processes – is the rate of return. At this point the utilization of the algal oil is not sufficient on its own, but the alga cells contain compounds that can be used in pharmaceutics (carotinoids), biogas synthesis (starch, sugars) or even in the agricultural industry (mirco and macro elements).

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