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MICROALGAE AS EFFICIENT FEEDSTOCK FOR BIOREFINERY

Abstract:
The global energy demand keeps rising and easy accessible fossil fuel reserves are gradually decreasing which leads to increasing interest in renewable energy sources. The energy production can be based on various sources alternative to petroleum, but the material economy mainly depends on biomass, in particular plant biomass. The potential of renewable biomass resources conversion to chemicals is sufficient to replace fossil crude oil as a carbon resource. In recent years it has increasingly become clear that first generation biofuels have got comparably unfavorable energy balances and therefore most likely can never play a major role in global energy supply. Lignocellulosic biomass is much cheaper for biofuel production than first generation feedstock, but still there are no efficient treatment technologies for large-scale applications. The microalgae might be the future source of biofuels and chemicals production. Microalgal lipids and carbohydrates could be converted to biofuels and the rest of microalgal biomass contains many valuable components, all of which are worth developing into refined products for various applications.

Key words:
microalgae, biorefinery, biofuels

Concept of biorefinery

The global energy demand keeps rising at a dramatic speed since the beginning of the industrial revolution in the late 18th century. In contrast, easy accessible fossil fuel reserves are gradually decreasing which leads to increasing energy prices [1]. The maintenance and management of resources are the fundamental political areas within sustainable development. Sustainable development requires safe and sustainable resources for industrial production [2]. First of all a search for new solutions to decrease present rapid consumption of non-renewable, fossil resources is required. Growing concerns over the availability and cost of extracting fossil fuel resources have stimulated the interest in renewable resources. Energy production can be based on various, alternative to petroleum, natural gas and coal, raw materials such as wind, sun, water and biomass but the material economy mainly depends on biomass, in particular plant biomass. In the near future it will be necessary to shift the economy from crude oil to biological raw materials. This radical change requires completely new approaches in research and development, production and economy. The factor that stimulates this revolution is the growing awareness of human influence on global climate and consequences that it brings to environment and economy. Reducing anthropogenic greenhouse gas (GHG) emissions is increasingly proposed as one of the key components in achieving global sustainable development goals. Such steps affect world economy and raise the interest in producing numerous necessary chemicals from renewable biomass resources [3].

The potential of renewable biomass resources conversion to chemicals is sufficient to replace fossil crude oil as a carbon resource. Success will depend on how far it is possible to change today's production of goods and services gradually from fossil to biological raw materials. Biological and chemical sciences will play a leading role in the generation of future industries and new synergies between biological, physical, chemical and technical sciences have to be elaborated and established. The whole process will be combined with new traffic technologies, media and information technologies and economic and social sciences [2].

A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power and chemicals from biomass [3, 4]. It combines the technologies between biological raw materials and the industrial intermediates and final products. Biorefineries can use a variety of biomass materials and through a series of conversion and separation steps yield bulk and specialty chemicals and materials. The principal goal in the development of biorefineries is defined by the following: (biomass) feedstock-mix + process-mix → product-mix. The classification of biorefineries can be done according to several criteria: either by feedstock materials, resulting products, technologies utilized or a combination of all three categories [Tab. 1]. In fact, the way these categories are combined accounts for the complexity of integrated biorefineries [2,3].

Tab. 1 Proposed criteria of biorefineries classification (based on [3])

Key chemical composition of biomass feedstock	➔	Technologies and unit operations	➔	Resulting products
• Carbohydrates		• fermentation		• materials
• lipids		• gasification		• biofuels
• proteins		• pyrolysis		• chemicals
• lignocellulosic		• hydrothermal liquefaction		• and intermediates
		• hydrogenation		• biogas
		• hydrothermolysis		• electricity
		• oxidation		• heat
		• hydrodeoxygenation		

Currently, chemicals that are produced from biomass in the largest volumes are identified as the first and second generation biofuels: bioethanol (over 88 billion liters in 2013), biodiesel and biogas [5]. Biomass is currently the only renewable carbon resource that could replace fossil ones, its availability and sustainability of is of crucial importance. Sustainability concerns that have arisen include the impact of biofuels on climate and the extent to which they can be utilized without causing significant and irreversible harmful environmental and social effects. Biorefineries need to select their feedstock for chemicals production avoiding direct competition with food and the next generation biofuel production. Forest and agricultural residues, industrial and urban side and waste streams, as well as algae are considered more suitable options. Production of various chemicals from biomass instead of fossil resources requires a paradigm change [2,3]. Profit of the biorefinery may differ depending on the geographic location and on feedstock available as well as the products, selected technologies and sequence of unit operations.

First, second and third generation of feedstock for biorefinery

Biofuels produced from sugar, grain and oleaginous crops are known as the first generation biofuels. The first generation feedstock has significant limitations and raises issues with regard to food versus fuel. Ethanol is the main currently produced biofuel. Most of production uses sugar- and starch-based feedstocks that have high biofuel conversion efficiency. However, sugarcane, the major sugar-based feedstock, requires tropical or temperate climates, with Brazil the only successful example of sugarcane ethanol use [6]. Starchbased feedstocks are mostly grains, that are not sustainable for biofuel production because of interference with food and feed market. For example, fuel ethanol production in the United States consumes one third of the corn harvest of the US causing a significant increase in global grain prices [7]. A similar situation also applies to biodiesel produced mostly from vegetable oils. Palm trees have the highest oil yield among oleaginous plants but much like sugarcane, are limited to tropical regions, while other oil plants such as soybeans, peanuts and rapeseeds are more widespread [8]. In recent years it has become clear that first generation biofuels such as ethanol production from plant sugars or biodiesel production from plant lipids have got comparably unfavorable energy balances and therefore most likely can never play a major role in global energy supply [1]. Systematic analysis of GHG balances show that agricultural crops (barley, turnip, rape) may produce higher levels of GHG than fossil fuels [9].

Lignocellulosic biomass, such as agricultural and forest residues, is not food-related and abundantly available at low cost without competition for arable land. It has been widely acknowledged as an ideal feedstock for the sustainable production of biofuels. The second generation biofuels, which convert a whole plant (e.g. biomass-to-liquid or biogas fermentation) offer far greater potentials than the first generation biofuels [10]. Lignocellulosic biomass is much cheaper for biofuel production than the first generation feedstock. However, due to its recalcitrance to degradation, lignocellulosic biomass still cannot be converted to biofuels in an efficient and cost-effective way [11]. The crystalline structure prevents enzymes - cellulases from binding onto cellulose surfaces to liberate sugars for biofuel production. An energy-intensive pretreatment and significant amounts of chemicals are needed to deconstruct it and even than the cost of cellulases required for the effective cellulose saccharification is much higher than of amylases and glucoamylases used for starch decomposition. Other obstacles include inefficient fermentation of pentose from hemicelluloses and the fact that lignin part is very difficult to ferment. This decreases the overall biomass to biofuels yield and causes higher waste treatment costs [8]. The overall assessment of sustainability is complicated by the fact that the carbon footprint of cultivation differs significantly among locations [12]. The cultivation emissions of N_2O can be responsible for more than 50% of the contribution to GHG emissions [3, 13]. However, there are first examples of successful introduction of the second generation biofuel production. The intensive research in biomass treatment technologies allowed to upgrade widely known processes like pyrolysis and Hydrothermal Liquefaction (HTL). Pyrolysis is a process of degradation at high temperature in the absence of oxygen or air. This process in its slow form has been used for hundreds of years to produce e.g. tar from pine and spruce. HTL is a technique for obtaining clean bio-oil and water insoluble fractions from biomass in the presence of a solvent or water. HTL of biomass has been studied for a little over 40 years. Both pyrolysis and HTL can virtually accept any form of biomass. In practice, woody biomass has been most often subjected to pyrolysis and wet biomass, like algae and manure, has been more widely treated with HTL. Several HTL studies are focused on different algae [14]. The high lipid content of algae makes it possible to produce bio-oil with energy content as high as the fossil reference values. Currently both technologies are expensive in large scale applications. The commercialization of pyrolysis technology is in its final phase: the technology has a wide patent coverage owned by UOP/Honeywell, the required fast fluidized bed installations are available from several producers [3]. The first large scale facility for woody biomass that is planned to produce 50,000 tons of bio-oil annually is under commissioning by Fortum, Finland. The initial intention is to replace the fuel oil used at Fortum's own heat plants with the bio-oil made from forest residues and other wood-based biomass [15]. The company announced that in the future, bio-oil could also be used as traffic fuel or as raw material for various biochemicals. Other Finnish companies: St1, Green Fuel Nordic, Vapo and UPM are also planning new biorefineries for the production of biofuels for traffic [16, 17, 18, 19]. The technologies for the second generation bio-oil based on woody biomass is currently commercialized in Finland while cellulosic ethanol production is in upscaling/commercialization phase in the USA. Several companies: Abengoa Bioenergy, BlueFire Ethanol, Coskata, DuPont Danisco Cellulosic Ethanol LCC, Iogen, Mascoma, POET, Range Fuels, SunEthanol, Verenium, ZeaChem, are commercializing or already producing cellulosic ethanol.

The third generation biofules are produced from algae biomass or by algae itself. Using microalgal feedstock for biofuel production has several advantages over traditional feedstock [8]. These include:

1. High growth rate and high area (or volumetric) productivity.
2. Absence of lignin and low hemicellulose content, and thus only minor pretreatment being needed.
3. Efficient CO_2 capture via photosynthesis, thereby mitigating greenhouse gas emissions.
4. Efficient light use and possibility of continuous production regardless of the season and climate.
5. Ability to grow on salt or wastewater streams, thereby reducing freshwater use.
6. Ability to use domestic, municipal or industrial wastewater as source of nutrients thereby reducing costs and partially removing contaminants from wastewater.
7. Ability to grow in areas unsuitable for agricultural purposes (e.g. desert and seashore lands), and thus there is no competition with arable land for food production.
8. Having a very short harvesting cycle (1–10 days) compared with other feedstock (which are harvested once or twice a year), thus providing enough supplies to meet sustainable biofulel production demand.

9. Production of algae feedstock is possible on relatively small area in the vicinity of processing plants.
10. Compatibility with integrated production of fuels and co-products within biorefineries.

These advantages allow microalgae to be preferentially selected as clean, efficient and sustainable feedstock for biofuel production e.g. bioethanol and have attracted several oil companies, such as Exxon, BP, Chevron, Shell and Neste Oil, to invest in this area [20]. Moreover, the production of microalgal biofuels for large scale is relatively close to being economically feasible. Companies like Algenol, Cellana, Solazyme, have already been producing 100% algae-derived biofules [21, 22, 23, 24]. Many other companies and projects aim at efficient production of biofuels and other chemicals form algae, utilization of waste CO_2, and other issues associated with upscaling to industrial scale production. Solazyme introduced renewable aviation fuel Solajet™ refined from algal oil. It is the world's first microbially-derived jet fuel to meet key industry specifications for commercial aviation[23].

Waltz [24] reported that reasonable productivity claims for oil production were ~20000 L oil $ha^{-1}yr^{-1}$ (~2000 gal oil $ac^{-1}yr^{-1}$) at present, and reasonable estimated productivity of future commercial systems might be ~60000 L oil ha^{-1} yr^{-1} (~6000 gal oil $ac^{-1}yr^{-1}$). These estimates were again supported by a panel representing some of the largest microalgal biofuel start-up companies at the 5th Algae Biomass Summit [25]. Potential yields of up to ~100,000 L $ha^{-1}yr^{-1}$ are theoretically possible at high irradiances (approximately 5% PCE at 25MJ $m^{-2}d^{-1}$ irradiance yields, 50g biomass dry weight m^{-2} d^{-1} at 50% oil content, or equivalent) but this will be difficult to attain in practice [26]. In addition to the microalgal lipids and carbohydrates that could potentially be converted to biofuels, the biomass of microalgae also contains many other valuable components, including polyunsaturated fatty acid, pigments and proteins, all of which are worth developing into refined products for various applications [24, 27].

All biomass components comparing to fossil fuels contain higher percentages of oxygen, with e.g. cellulose containing about 50-52 wt% oxygen and correspondingly lignin 28-33 wt% oxygen [28]. On the one hand the further the ratios are from fossil reference values the more reactions (e.g. hydrotreatment, hydrodeoxygenation) are required to find pathways to produce the same type of products as current petroleum refineries do today. On the other hand higher oxygen to carbon ratios offer also new possibilities to produce oxygen containing molecules like butanol, methyltetrahydrofuran (MTHF) and ethers [29]. Oxygen-rich monomers like carboxylic acids (lactic acid, succinic acid, itaconic acid and levulinic acid) are gaining interest as biopolymers [30]. Also several other chemical routes to utilize succinic acid are recognized [3, 31].

Microalgae cultivation

Microalgal biomass cultivation is regarded as a potential way to overcome our current reliance on fossil fuels for a number of reasons, such as high area yields compared with other crops, high oil contents in some strains, low water consumption rates, and the possibility of producing microalgae on infertile lands [32] . There are several problems that need to be solved during the development of microalgae-based biorefinery technologies [24]. The most challenging problems for the microalgae industry include:

1. high installing and operating cost,
2. difficulty in controlling the culture conditions,
3. contaminating bacteria or alien algae,
4. unstable light supply and weather.

It is of great importance to isolate good microalgae/cyanobacteria strains that are rich in target products, tolerate high (or low) temperature, and easily become predominant in the culture environment. Obtaining good microalgae strains is the key factor leading to stable and sustainable microalgae cultivation, which is extremely important in industrial applications of microalgae. The next challenge is identification of preferable culture conditions for improving target-product production. Designing efficient and economically feasible microalgae cultivation system (or photobioreactors) is also critical to improve the productivity of microalgal biomass or of target products [33]. Accumulation of different components (such as lipids, carbohydrates, proteins and pigments) in microalgae requires different cultivation conditions and operation strategies. To achieve this more understanding of the photosynthetic metabolism and physiology of the microalgae used, development of more advanced engineering technology to produce efficient photobioreactors for microalgae growth and product formation are necessary.

The choice of sustainable algal species is made on the basis of the following criteria [34, 35]:
1. The type of fuel/product to be produced.
2. The most suitable chemical composition of biomass and content of dry matter.
3. The method of cultivation that will be favorable under the local climatic conditions.
4. The media fulfilling nutrient requirements of a given species of algae.
5. Rate of growth of the species measured as the amount of biomass produced in a given time.
6. Ecological tolerance of the species (to temperature, pH, salinity, elevated saturation with oxygen).
7. Behavior in a culture with high population density,
8. Structure and size of cell,
9. Possibility of acquiring other valuable substances from a given species.

From a biorefinery point of view, the most important process conducted by algae is photosynthesis. In this process algae convert the energy of photons (light) in to the energy enclosed in chemical bonds of organic compounds. Photosynthesis is comprises reactions taking place in the presence of light (light phase) and the that taking place in darkness (dark phase). For correct energy conversion, cultivation conditions must take into account both phases of photosynthesis. It has been calculated that the energy which reaches the earth's surface equals to around 5600 times the global energy demand today [1, 36]. The distribution of solar energy is not uniform across the globe, and some regions are better suited for solar technologies than others. Only about 43-45% of the light radiation spectrum is photosynthetically active and furthermore the theoretical efficiency of photosynthetic light energy conversion into chemical energy is 11% [37]. Under dark conditions algae use up the stored energy for respiration. Depending on conditions, up to 25% of biomass produced during the day may be consumed again during the dark period [34, 38].

It has been argued that metabolic generation of biomass theoretically can achieve photosynthetic conversion efficiency of ~8% of the full solar spectrum [39] even with genetic improvement. Some modeling has therefore explored production at PCE rates up to 10% for photosynthesis to biomass [40, 41], but they rather support the view that these are unlikely to be achievable for individual native species. Other reports suggest that higher efficiency is possible for fuels such as H_2 [42], the production of which is closely coupled to the photosynthetic electron transport chain and avoids the inefficiencies associated for example with oil biosynthesis. Furthermore, mixed cultures of green microalgae, cyanobacteria and purple bacteria collectively have a broader absorption range, which in theory could yield a higher photon-to-chemical-energy-conversion efficiency. The expected maximum performance for open ponds is a photo-conversion efficiency (PCE) of around 0,5–1%, thus comparable to that of terrestrial energy plants such as maize or sugarcane. Microalgal dry biomass concentrations usually do not exceed 20g L^{-1}. Currently, for microalgal biomass production, levels of~2% PCE are achievable in conventional high rate pond (HRP) systems, and higher levels of~4.5% are reportedly achievable in photobioreactors (PBRs) [26]. The natural sunlight can be supplemented or replaced with artificial light sources like fluorescent tubes or LEDs (light-emitting diodes). The latter ones have a significant advantage, a possibility of precise wavelengths adjustment and production of photosynthetically active radiation. Yet both light sources are currently economically inefficient for large scale algae production. Productivity modeling for microalgal production systems at different geographic locations demonstrates the potential yields of biomass [43,44]. For Germany, a reported light energy input of 1000 kWh m^{-2} yr^{-1} (~14,4MJ m^{-2} d^{-1}) over 250 operational days to account for productivity losses during winter concluded that the system could yield 40T ha^{-1} yr^{-1} at 2,4% PCE, (equivalent to a productivity level of 16g m^{-2} d^{-1}) [45]. More tropical climes with light intensity of 25MJ m^{-2} d^{-1} and 330 operational days per year (allowing one month of down time) would yield 89T ha^{-1} yr^{-1} at 2.4% PCE. The corresponding production levels assuming 5% PCE would therefore rise to 83T ha^{-1} yr^{-1} (at 14,4MJ m^{-2} d^{-1}) and 185T ha^{-1} yr^{-1} (at 25MJ m^{-2} d^{-1}). In summary, current yields are estimated to range between ~40 and 90T ha^{-1} yr^{-1}, and these might sensibly be expected to rise towards ~80–185T ha^{-1} yr^{-1}, based on these data. Theoretically, further improvement is possible in the time frame towards 2050 [26].

Proper illumination of an algal culture is only one aspect necessary for the photosynthesis to proceed efficiently. If the concentration of oxygen in a growth medium is high and the concentration carbon dioxide is low photorespiration can take place, which may lower the efficiency of photosynthesis by as much as 50%, depending on a species of algae. Photorespiration is a process similar to the mitochondrial respiration, but it takes place in chloroplasts, in the presence of light, and "wastes energy" by absorbing oxygen and evolving carbon dioxide. The culture should be artificially supplemented with carbon dioxide and, at the same time, excess of oxygen produced should be removed. Photorespiration may be induced by high temperature and high light intensity [46, 47]. The relation between the rate of growth of algal cells and the intensity of light is also nonlinear. Up to a certain, relatively low, light intensity the growth of cells is directly proportional to increase in light intensity. Most algal species react in this way up to light intensity of ca. 200 µE m^{-2} s^{-1} while higher light intensity slows down the growth. Still higher light intensity causes excessive excitation and, consequently, inactivation and destruction of the PSII system. This light-induced reduction in the photosynthetic capacity is called photoinhibition, and result in decrease of productivity. Light is absorbed by algae, but with increase in their density in a culturing container that absorption gets weaker. Thus, to ensure stable and repeatable illumination conditions is important. That problem is best solved by the use of photobioreactors which allow to control the culturing conditions much better than in open ponds [34].

The optimum pH for the cultivation of many algal species ranges from 7 to 9. During growth pH increases due to the absorption of CO_2 in the process of photosynthesis and can reach very high values, even up to 11. This should be kept in mind and pH should be maintained at a stable level, e.g. through supplementation with CO_2. In 99.9% algae biomass consists of six main elements: carbon (C), oxygen (O), hydrogen (H), nitrogen (N), sulphur (S) and phosphorus (P) while Calcium (Ca), potassium (K), sodium (Na), chlorine (Cl), magnesium (Mg), iron (Fe) and silicon (Si) appearing in smaller amounts. Other elements occur in trace amounts as they are only used in catalytic reactions [34, 46].

Photoautotrophic algae absorb carbon from the aqueous solution in the form of, CO_2, H_2CO_3, HCO_3^- and CO_3^{2-} and build it into hydrocarbons during photosynthesis. Mixotrophic or heterotrophic algae absorb simple organic substances like glucose, organic acids, acetic acid, lactic acid, alcohols or amino acids [48] instead of CO_2. The cultivation of microalgae for energy generation should be based on photoautotrophic nutrition, even if only for ecological reasons. Algae are capable of absorbing 1,65-1,83g of carbon dioxide per 1g of biomass produced [49], which might contribute to a considerable reduction of the content of that greenhouse gas in the atmosphere. The content of the CO_2 in atmosphere is ~0,04% and does not ensure efficient growth of algal biomass, and is definitely insufficient to stimulate fast growth rates and high productivity of microalgae, required for the large scale production of biofuels. Therefore, supplementation of cultures with carbon dioxide is necessary, at concentrations from several to even several dozen percent. CO_2 can originate not only from atmosphere but from industrial gases as well. Culture can be also supplemented with soluble carbonates. For efficient growth, microalgae require at least 1% of CO_2 in the atmosphere. Certain species of microalgae are characterized by good tolerance to high concentrations of CO_2 up to 18% [50, 51]. Gases from the processes of combustion contain usually up to 15% CO_2 and are capable of providing sufficient amounts of CO_2 for large-scale production of microalgae and mitigate the emission of this green house gas [34, 52]. Microalgae-based CO_2 fixation is much faster and more efficient than that of terrestrial plants (around 10–50 times higher), it has thus been considered to have the potential to serve as a commercially feasible process for mitigation of CO_2 emissions [24, 53]. Concentration of CO_2 strongly influences the fatty acid content and profiles in algal cells.

Nitrogen can constitute 10% or more of dry matter of algal biomass, depending on the species, culturing conditions and its availability for the cells. Nitrogen can be supplied to algae in the form of: nitrates (NO_3^-), nitrites (NO_2^-) ammonium (NH_4^+), urea and amino acids. The uptake of nitrogen compounds form the medium may significantly influence the pH of the medium. Additionally some species of cyanobacteria (blue-green algae) are able to differentiate vegetative cells into heterocysts that bind atmospheric nitrogen (N_2). This process is energy consuming and occurs in absence of extracellular bioavailable sources of nitrogen. All forms of nitrogen are intracellularily transformed into ammonium, which is the only form that is utilized by a cell to produce amino acids. Therefore, from the energy point of view, the most favorable is direct use of the ammonium form of nitrogen for algae nutrition [34, 54].

Biomass of microalgae contains up to 1-1,2% of phosphorus in its dry matter [54]. Algae absorb phosphorus supplied as orthophosphoric ions $H_2PO_4^-$ and HPO_4^{2-}. Phosphorus often disappears from the substrate already in the initial phase of cultivation and is accumulated by cells. Even though the level of phosphorus in the substrate is very low, the growth rate of the culture remains high. Elements such as nitrogen (N) and phosphorus (P) can be supplied to cultures in the form of an agricultural fertilizer, which is simple, easily available, but may notably increase the costs of algae cultivation [55]. There are several options of cheaper sources of those elements like sewage from fisheries [56], and from pigsties [57] or residues after various technological processes, e.g. anaerobic fermentation or gasification [34, 58]. In addition recycling of water used during microalgae cultivation processes is an advantage [24].

Stirring is very important during algae cultivation. Its primary function is to maintain algal cells in suspension. It is also responsible for the distribution of nutrients and heat, it improves the transfer of CO_2 and flow between cells, it removes oxygen formed during photosynthesis, facilitates the flow of cells to the best illuminated parts of the photobioreactor and reduces the risk of photoinhibtion [34, 59].

Finally, life cycle analysis (LCA), energy balance and cost assessment should be also performed to justify the economic feasibility and environmental impacts. Biomass is a carbon neutral source only when emissions from biomass use are re-absorbed into the re-growth of new biomass. Uncertainties of these emissions are recognized, and their influence on final outcomes needs sensitivity analysis. The highest uncertainty relates to the N_2O emissions from nitrogen fertilization and to carbon stock changes. Also, transport of feedstock has an impact on the GHG emissions. The impact of transport could be reduced by small scale production without loss of GHG benefits or by reducing the transport volume by decentralized pyrolysis of plants that convert e.g. wood chips into liquid form [60]. Overall, the benefits of decentralized production depend on the size of the territory wherefrom the raw material is collected [3, 61].

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References

[1] J.H. Mussgnug, V. Klassen, A. Schlüter, O. Kruse Microalgae as substrates for fermentative biogas production in a combined biorefinery concept, Journal of Biotechnology 150 (2010) 51–56
[2] B. Kamm . M. Kamm Principles of biorefineries Appl Microbiol Biotechnol 64 (2004) 137–145
[3] R. Kajaste Chemicals from biomass - managing greenhouse gas emissions in biorefinery production chains a review, Journal of Cleaner Production 75 (2014) 1-10
[4] NREL, 2014. http://www.nrel.gov/biomass/ integrated _biorefinery.html,
[5] http://www.ethanolrfa.org/pages/ethanol-facts-environment
[6] J. Goldemberg, Ethanol for a sustainable energy future, Science 315 (2007) 808–810.
[7] (13) R.L. Naylor, A.J. Liska, M.B. Burke, W.P. Falcon, J.C. Gaskell, S.D. Rozelle, K.G. Cassman, The ripple effect: biofuels, food security, and the environment, Environment 49 (2007) 30–43.
[8] C.Y. Chen, X.Q. Zhao, H.W. Yen, S.H. Ho, C.L. Cheng, D.J. Lee, F.W. Bai, J.S. Chang 'Microalgae-based carbohydrates for biofuel production Biochemical Engineering Journal 78 (2013) 1– 10
[9] K. Koponen, S. Soimakallio, E. Tsupari, R. Thun, R. Antikainen, GHG emission performance of various liquid transportation biofuels in Finland in accordance with the EU sustainability criteria. Appl. Energy 102 (2013) 440-448.
[10] IEA, 2010. Sustainable Production of Second-Generation Biofuels (Report). http://www.iea.org/papers/2010/second generation biofuels.pdf.
[11] (16) M.E. Himmel, S.Y. Ding, D.K. Johnson, W.S. Adney, M.R. Nimlos, J.W. Brady, T.D. Foust, Biomass recalcitrance: engineering plants and enzymes for biofuels production, Science 315 (2007) 804–807.
[12] Y. Gan, C. Liang, W. May, S.S. Malhi, J. Niu, X. Wang,. Carbon footprint of spring barley in relation to preceding oilseeds and N fertilization. Int. J. Life Cycle Assess. 17 (2012) 635-645.
[13] A. Ekman, P. Börjesson, Life cycle assessment of mineral oil-based and vegetable oil-based hydraulic fluids including comparison of biocatalytic and conventional production methods. Int. J. Life Cycle Assess. 16 (2011) 297-305.
[14] U. Jena, K.C. Das, J.R. Kastner, Effect of operating conditions thermochemical liquefaction on biocrude production from *Spirulina platensis*. Bioresour. Technol. 102:10 (2011) 6221-6229.
[15] http://www.fortum.com/en/energy-production/fuels/pages/default.aspx
[16] http://www.st1.eu/
[17] http://www.greenfuelnordic.fi/en/page/2
[18] http://www.vapo.fi/en
[19] http://www.upm.com/en/Pages/default.aspx
[20] A. Mascarelli,. Gold rush for algae, Nature 461(2009) 460–461.
[21] http://www.algenol.com/
[22] http://cellana.com/
[23] http://solazyme.com/solutions/fuel/?lang=en
[24] E. Waltz, Biotech's green gold? Nat. Biotechnol. ,27:1 (2009) 15–18. [25] J.R. Benemann, J. Olivares, S. Mayfield, J. Kneiss, G. Dirks, M. Sabarsky, An update on the global consortia, 5th Algae Biomass Summit: Algae

Biomass Summit Plenary Panel. Minneapolis, USA.(2011.10.26.). [26] E. Stephens, L. Wagner, I.L. Rossand, B. Hankamer, Microalgal production systems: Global impact of industry scale-up. [In] C. Postenand, C. Walter, (Eds.) Microalgal Biotechnology: Integration and Economy De Gruyter, Berlin, 2012

[27] T.M. Lammens, M.C.R. Franssen, E.L. Scott, J.P.M. Sanders, Availability of protein-derived amino acids as feedstock for the production of bio-based chemicals. Biomass Bioenergy 44(2012) 168–181.

[28] A. Nzihou, G. Flamant, B. Stanmore,. Synthetic fuels from biomass using concentrated solar energy e a review. Energy 42 (2012) 121-131.

[29] K. Meli, M. Hurme, Evaluation of lignocellulosic biomass upgrading routes to fuels and chemicals. Cellul. Chem. Technol. 44:4-6 (2010) 117-137.

[30] K. Yao, C. Tang, Controlled polymerization of next-generation renewable monomers and beyond. Macromolecules 46:5 (2013) 1689-1712.

[31] C. Wang, A. Thygesen, Y. Liu, Q. Li, M. Yang, D. Dang, Z. Wang, Y. Wan., W. Lin, J. Xing,. Bio-oil based biorefinery strategy for the production of succinic acid. Biotechnol. Biofuels 6:74 (2013) 1-10

[32] E. Stephens, I.L. Ross, Z. King, J.H. Mussgnug, O. Kruse, C. Posten, M.A. Borowitzka, B. Hankamer,. An economic and technical evaluation of microalgal biofuels. Nat. Biotechnol. 28 (2010) 126–128.

[33] Y.L. Cheng, Y.C. Juang, P.W. Tsai, S.H. Ho, C.Y. Chen, J.S. Chang, W.M. Chen, J.M. Liu, D.J. Lee,. Harvesting of *Scenedesmus obliquus* FSP-3 using dispersed ozone flotation. Bioresour. Technol. 102 (2011) 82–87.

[34] E. Kwietniewska, J. Tys, I. Krzemińska, W. Kosieł, 2012 Microalgae – cultivation and application of biomass as a source of energy: a review. Acta Agrophysica monographiae 2 (2012) 1-108

[35] T.M. Mata, A.A. Martins, N.S. Caetano,. Microalgae for biodiesel production and other applications: a review. Renewable and Sustainable Energy Reviews, 14 (2010) 217-232.

[36] P.M. Schenk, S.R. Thomas-Hall, E. Stephens, U.C. Marx, J.H. Mussgnug, C. Posten, O. Kruse, B. Hankamer,. Second generation biofuels: high-efficiency microalgae for biodiesel production. BioEnergy Research 1 (2008) 20–43.

[37] K.S. Gao, Y.P. Wu, G. Li, H.Y. Wu, V.E. Villafane, E.W. Helbling,. Solar UV radiation drives CO2 fixation in marine phytoplankton: A doubleedgedsword. Plant Physiol., 144:1 (2007), 54-59.

[38] Chisti Y., 2007. Biodiesel from microalgae. Biotechnol. Adv., 25, 294-306.

[39] X.G. Zhu, S.P. Long, D.R. Ort, What is the maximum efficiency with which photosynthesis can convert solar energy into biomass? Curr. Opin. Biotechnol.,19:2 (2008) 153–159.

[40] E. Stephens, I.L. Ross, Z. King, J. Mussgnug, O. Kruse, C. Posten, M.A. Borowitzka, B. Hankamer, An economic and technical evaluation of microalgal biofuels. Nat. Biotechnol.,28:2 (2010) 126–128.

[41] P.J.le.B. Williams, L.M.L. Laurens, Microalgae as biodiesel and biomass feedstocks: review and analysis of the biochemistry, energetics and economics, Energy Environ.Sci.,3:5 (2010) 554–590.

[42] A. Melis, Solar energy conversion efficiencies in photosynthesis: minimizing the chlorophyll antennae to maximize efficiency. Plant. Sci., 177:4 (2009) 272–280.

[43] K.M. Weyer, D.R. Bush, A. Darzins, B.D. Wilson, Theoretical maximum algal oil production, Bioenergy.Res., 3:2 (2010) 204–213.

[44] A. Franz, F. Lehr, C. Posten, G. Schaub, Modeling microalgae cultivation productivities in different geographic locations – estimation method for idealized photobioreactors, Biotechnology Journal 7:4 (2012) 546–557.

[45] C. Wilhelm, T. Jakob From photons to biomass and biofuels: evaluation of different strategies for the improvement of algal biotechnology based on comparative energy balances. Appl. Microbiol. Biotechnol., 92:5 (2011) 909–919.

[46] L. Barsanti, P. Gualtieri,. Algae: anatomy, biochemistry, and biotechnology, CRC Press, USA 2006.

[47] J. Masojidek, M. Koblizek, G. Torzillo,. Photosynthesis in microalgae. In: Handbook of microalgal culture: Biotechnology and Applied Phycology (ed A. Richmond), Blackwell Publishing Ltd, Oxford, UK. 2004 20 - 39.

[48] Y.K. Lee,. Heterotrophic carbon nutrition. In: Handbook of microalgal culture: biotechnology and applied phycology (ed A. Richmond), Blackwell Publishing Ltd, Oxford, UK, 2004 116-124.

[49] J. Doucha, F. Straka, K. Lívanský, Utilization of flue gas for cultivation of microalgae (*Chlorella* sp.) in an outdoor open thin-layer photobioreactor, J Appl Phycol., 17 (2005) 403-412

[50] M. Matsumoto, Y. Hiroko, S. Nobukazu, O. Hiroshi, M. Tadashi, Saccharification of marine microalgae using marine bacteria for ethanol production. Appl. Bioch. Biotech.,105 (2003) 247-254.

[51] M.G. de Morais, J.A.V. Costa, Biofixation of carbon dioxide by *Spirulina* sp. and *Scenedesmus obliquus* cultivated in a three-stage serial tubular photobioreactor. J. Biotechnol., 129 (2007) 439-445.

[52] A. Kumar, S. Ergas, X. Yuan, A. Sahu, Q. Zhang, J. Dewulf, F.X. Malcata, H. van Langenhove,. Enhanced CO_2 fixation and biofuel production via microalgae: recent developments and future directions, Trends in Biotechnology, 28:7(2010) 371-380.

[53] S.H. Ho, C.Y. Chen, , D.J. Lee,., J.S. Chang, Perspectives on microalgal CO_2- emission mitigation systems – a review. Biotechnol. Adv. 29 (2011) 189–198.
[54] C.S. Reynolds,. The ecology of phytoplankton. Cambridge University Press, UK, 2006. [55] Y. Chisti,. Response to Reijnders: Do biofuels from microalgae beat biofuels from terrestrial plants?, Trends Biotechnol., 26:7 (2008) 351-352.
[56] M. Aresta, A. Dibenedetto, G. Barberio,. Utilization of macro-algae for enhanced CO2 fixation and biofuels production: development of a computing software for an LCA study. Fuel Process. Technol., 86:14-15(2005) 1679-1693.
[57] E.J. Olguín, S. Galicia, G. Mercado, T. Pérez,. Annual productivity of *Spirulina* (*Arthrospira*) and nutrient removal in a pig wastewater recycling process under tropical conditions, Journal of Applied Phycology, 15:2 (2003), 249-257.
[58] T. Minowa, S. Sawayama,. A novel microalgal system for energy production with nitrogen cycling. Fuel, 78 (1999)1213-1215.
[59] M. Janvanmardian, B.O. Palsson, High density photoautotrophic algal cultures: design, construction and operation of a novel photobioreactor system. Biotechnol. Bioeng., 38 (1991) 1182-1189
[60] P. Haro, F. Trippe, R. Stahl, E. Henrich, Bio-syngas to gasoline and olefins via DME-A comprehensive techno-economic assessment. Appl. Energy 108 (2013) 54-65.
[61] L. Iglesias, A. Laca, M. Herrero, M. Díaz,. A life cycle assessment comparison between centralized and decentralized biodiesel production from raw sunflower oil and waste cooking oils. J. Clean. Prod. 3 (2012) 162-171.

JEDNOKOMÓRKOWE GLONY JAKO SUROWIEC DLA BIORAFINERII

Streszczenie:

Światowy popyt na energię nieustannie wzrasta, a dostępne złoża paliw kopalnych stopniowo się wyczerpują, co przyczynia się do wzrostu zainteresowania odnawialnymi źródłami energii. Produkcja energii może być oparta na wielu alternatywnych paliwach, ale gospodarka materiałowa jest w głównej mierze oparta na biomasie, w szczególności pochodzenia roślinnego. Potencjał konwersji biomasy do użytecznych związków chemicznych jest wystarczający by zastąpić ropę naftową i węgiel. W ostatnich latach stało się jasne, że biopaliwa pierwszej generacji mają mało korzystny bilans energetyczny i prawdopodobni nigdy nie będą odgrywać znaczącej roli w globalnym rynku energetycznym. Lignocelulozowa biomasa jest znacznie tańszym surowcem do produkcji biopaliw, ale nadal nie opracowano wydajnych sposobów jej przetwarzania, które mogłyby znaleźć zastosowanie w produkcji przemysłowej na dużą skalę. Jednokomórkowe glony mogą stać się przyszłością zarówno biopaliw jak i produkcji szerokiej gamy związków chemicznych. Lipidy i węglowodany zawarte w ich komórkach stanowić mogą substrat do produkcji biopaliw, a pozostałą część biomasy zawierająca szereg cennych składników, można przetworzyć w rafinowane produkty o szerokim spektrum zastosowań.

Słowa kluczowe: glony, biorafineria, biopaliwo