CZECH UNIVERSITY OF LIFE SCIENCES PRAGUE

Faculty of Tropical AgriSciences

Biofuels production from algae: challenge and potential

Bachelor Thesis

Prague 2017

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Declaration

I hereby declare that this thesis entitled “Biofuels production from algae: challenge and potential” is my own work and all the sources have been quoted and acknowledged by means of complete references.

In Prague 21. 4. 2017

……………………………….

Kryštof Mareš

Acknowledgements

I would like to thank my supervisor Ing. Tatiana Ivanova, Ph.D. for her approach, cooperation, expert advices and support during writing and fulfilling my Bachelor's Thesis. At least but not last I would like to thank my family and friends for all support.

Abstract

Research in the field of algae-based biofuels in recent years has increased significantly, the most attractive is their potential in the way of replace fossil fuels. Algae are the fastest growing plants in the world and are considered as the most suitable and sustainable source of green energy. Biomass from algae offers a wide range of applications - currently in production of biofuels such as biodiesel and bioethanol, biohydrogen but also, biomethane, bio-oil and more. Algae also offer a large number of substances used in various industries from cosmetics and textiles to food processing.

This Bachelor’s Thesis titled "Biofuels production from algae: a challenge and a potential" was written as a literature review from scientific articles that have been obtained from famous professional databases. This Thesis summarizes research knowledge about algae, their distribution and cultivation in open ponds and photobioreactors. Individual types of cultivation technologies have their advantages and disadvantages, which are discussed. The Thesis focuses on the production of biofuels, especially biodiesel and bioethanol. It describes their pros and cons compared to other biofuel’s sources. The potential of biofuels from algae carries enormous challenges as research and overall use of algae concerned, while production of non-energy materials present a big prospect for using algae. Cultivation and use of algae for biofuels goes hand in hand with the production of non-energetic products, which are often far higher in economic utilization, and thus support the overall production of algae-based biofuels. The Thesis summarizes what challenge brings the algae for biofuels production, and describes potential that could be use in the nearest decades.

Key words: macroalgae, microalgae, biodiesel, bioethanol, open ponds, photobioreactors

Abstrakt

Výzkum ve směru biopaliv z řas v posledních letech výrazně vzrostl, nejzajímavějším se jeví jejich potenciál k nahrazení fosilních paliv. Vodní řasy jsou nejrychleji rostoucí rostliny na světě a jsou považovány za nejvhodnější a nejudržitelnější zdroj zelené energie. Biomasa z vodních řas nabízí široké využití právě ve výrobě biopaliv, jako jsou bionafta a bioetanol, ale také biovodík, biomethan, bio-olej a další. Vodní řasy nabízí také velké množství látek využívaných v různých odvětvích od kosmetiky přes textilní průmysl po potravinářství.

Tato bakalářská práce na téma: „Produkce biopaliv z řas: výzva a potenciál“ byla sepsána formou literární rešerše pouze z odborných článků, které byly získávány ze světových odborných databází. Práce shrnuje dosavadní poznatky o vodních řasách, jejich rozdělení a o pěstování vodních řas v otevřených nádržích a ve fotobioreaktorech. Jednotlivé typy technologií pěstování mají své výhody a nevýhody, které jsou v práci probrány. Dále se práce zaměřuje na výrobu biopaliv, především bionafty a bioetanolu, a popisuje jejich klady a omezení oproti jiným zdrojům biopaliv. Potenciál v biopalivech z vodních řas nese ohromné výzvy, co se výzkumu a celkového využití vodních řas týče. Zároveň produkce neenergetických látek nese ohromný potenciál k využívání vodních řas. Pěstování a využívání vodních řas pro biopaliva tak jde ruku v ruce s výrobou jiných produktů, které mají mnohdy daleko vyšší ekonomické využití, a tak podporují celkovou produkci „řasových biopaliv“. Práce prezentuje, jakou výzvu představují vodní řasy pro produkci biopaliv a vyličuje potenciál, který by se dal v příštích dekádách využít.

Klíčová slova: makrořasy, mikrořasy, biodiesel, bioetanol, otevřené nádrže, fotobioreaktory

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1. Introduction

In last decades biomass as source of energy is rising due to many reasons. The substitution of fossil fuels by biofuels appears to be an effective strategy to meet not only the future world energy demand but also the requirement for reducing greenhouse gasses and particularly carbon emissions originating mostly from fossil fuels combustion (Vassilev, 2016). Furthermore, other reasons could be independence on fossil fuels and countries with petroleum industry. EU countries have set mandatory minimal targets to reduce the threshold of their greenhouse gas emissions. Besides, in transport sector those countries set that 10% of the energy should be produced from renewable resources by 2020. The main advantage is that renewable resources (biomass) is worldwide availability due to its diversity of sources as vegetation, energy crops, animal fats, wood and agricultural residues, municipal and industrial wastes (Miret, 2016).

The production of biofuels is expected to grow steadily in the next few decades. Biomass energy is an important renewable energy source, representing 10.4% of the world's total primary energy supply or 77.4% of global renewable energy supply. Currently, some countries (for example, Brazil, Germany, Australia) already use biofuels such as bioethanol and biodiesel in relatively large scale and it is expected that, this trend will continue to develop and biofuels will expand in more countries (Suganya, 2016).

Macro and micro-algae offers a huge potential for the production of biofuels. If used in a sustainable way, algal biomass could be beneficial for the reduction of the world's dependency on oils, as well as the global emission of greenhouse gases (Sambusiti, 2015). The present Bachelor Thesis is focused on this topical issue.

2. Aim of the thesis

The objective of this Thesis was to summarize scientific information about biofuels production from algae with a focus on description and evaluation of different algae cultivation technologies as well as analysis of the main algae-based biofuels such as biodiesel and bioethanol. The specific aim of the work was also to highlight advantages, disadvantages and future prospects of algae technologies.

3. Methodology

The Thesis was written as literature review based on scientific articles. The search for scientific information was done by the keywords (algae cultivation, microalgae, macroalgae, biofuel, biodiesel, bioethanol, open ponds, photobioreactor, etc.) in scientific databases like ScienceDirect, Web of Science, EBSCO. The main journals referenced in the present work were Fuel, Renewable and Sustainable Energy Reviews, Bioresource Technology, Energy and others. Evaluation of algae cultivation technologies and produced biofuels was mainly based on summarisation of their advantages and disadvantages. Potential of other biofuels and non-energy products from algae was discussed, too.

4. Literature review

4.1. Biomass

Biomass could be distributed/processed into four generations of biofuels. First-generation biomass-based biofuels are produced from edible feedstocks such as sugar, seeds and oils, or plants as sugarcane, corn, sunflower, wheat, barley, soybean or oil palm. These biofuels made from food and feed crops cannot meet the demand because of unsustainability, inefficiency and inadequacy to fulfil rising requirements. There are controversial debates due to the ‘’food versus fuel’’ dilemma because this type of biomass affects global security, prices and food markets (Vassilev, 2016). Moreover, farmers wish to cultivate bioenergy crops instead of food crops due to high profits they incur but this also affects the food supply creating a situation of increased food prices. In addition, extensive cultivation of energy crops also raises concerns regarding pollution of agricultural land with fertilizers and pesticides, soil erosion, reduced crop diversity and causes the contamination of surface waters eventually leading to eutrophication and eco-toxicity (Sirajunnisa, 2016).

The second-generation biofuels are produced from non-edible crops (Vassilev, 2016). It was developed to reduce water consumption, utilities consumption in the transformation process and the competition with food crops (Miret, 2016). These biofuels bring more advantages comparing to the first-generation biofuels. They do not compete with food production and have higher yield and lower land requirements. Unfortunately, the limitations of first- and second-generation of biofuel resources shows that in the present they are inadequate to meet global demand for biofuels due to concerns over protection of global ecosystems and land availability (Vassilev, 2016).

The third-generation biofuels are produced from algae biomass as feedstock (Vassilev, 2016). The recent advent of third-generation biofuels from algae has been considered as a great sustainable alternative approach (Srinophakun, 2016). Algae-based fuel may overcome the major drawback associated with the first- and second-generation biofuels (Vassilev, 2016). Algae based biofuel production has very small degree of intrusion in the food versus fuel dispute of tomorrow which is an added advantage (Bharathiraja, 2015). However, the positive standpoints in terms of the economic, environmental and social aspects have not been sufficient at present to produce algae on a large commercial scale due to the high production costs (Vassilev, 2016).

The fourth-generation biofuels are sometime mentioned as part of third-generation biofuels. It is the youngest section of biofuels. It is based on microscopic organisms produced from genetically modified microbes, yeast, fungi, microalgae and cyanobacteria that convert CO_2 directly to fuel or modifying the oil-storing capabilities of organisms (Vassilev, 2016). Production of oil from microalgae was theoretically calculated to be 350 000 l/ha/yr. Compared with the production of another biomass resources as castor, coconut, palm, soybean or sunflower it is in some cases much more than 300 times higher yield of oil production (Srinophakun, 2016).

4.2. Algae

Algae are diverse group of photosynthetic organisms from unicellular (microalgae or phytoplankton) to multicellular (macroalgae or filamentous) living in both marine and freshwater environments. These simple chlorophylls containing organisms are able to photosynthetically convert sunlight, water and CO_2 to a wide range of metabolites and chemicals in algal biomass (Vassilev, 2016).

Microalgae contain abundant lipids, carbohydrates, proteins, fats and a variety of inorganic molecules. Figure 1 shows that some of the components can be converted into biofuels, while others can be extracted and processed into different valuable byproducts or co-products, such as cosmetics, pharmaceuticals and nutritious feed. Co-producing high values with biofuels can provide a promising opportunity to commercialize microalgal biofuels. The combination of microalgal biofuels production with the conventional applications is a bright solution to prospering the microalgal biorefinery industry in a sustainable manner (Zhu, 2015).

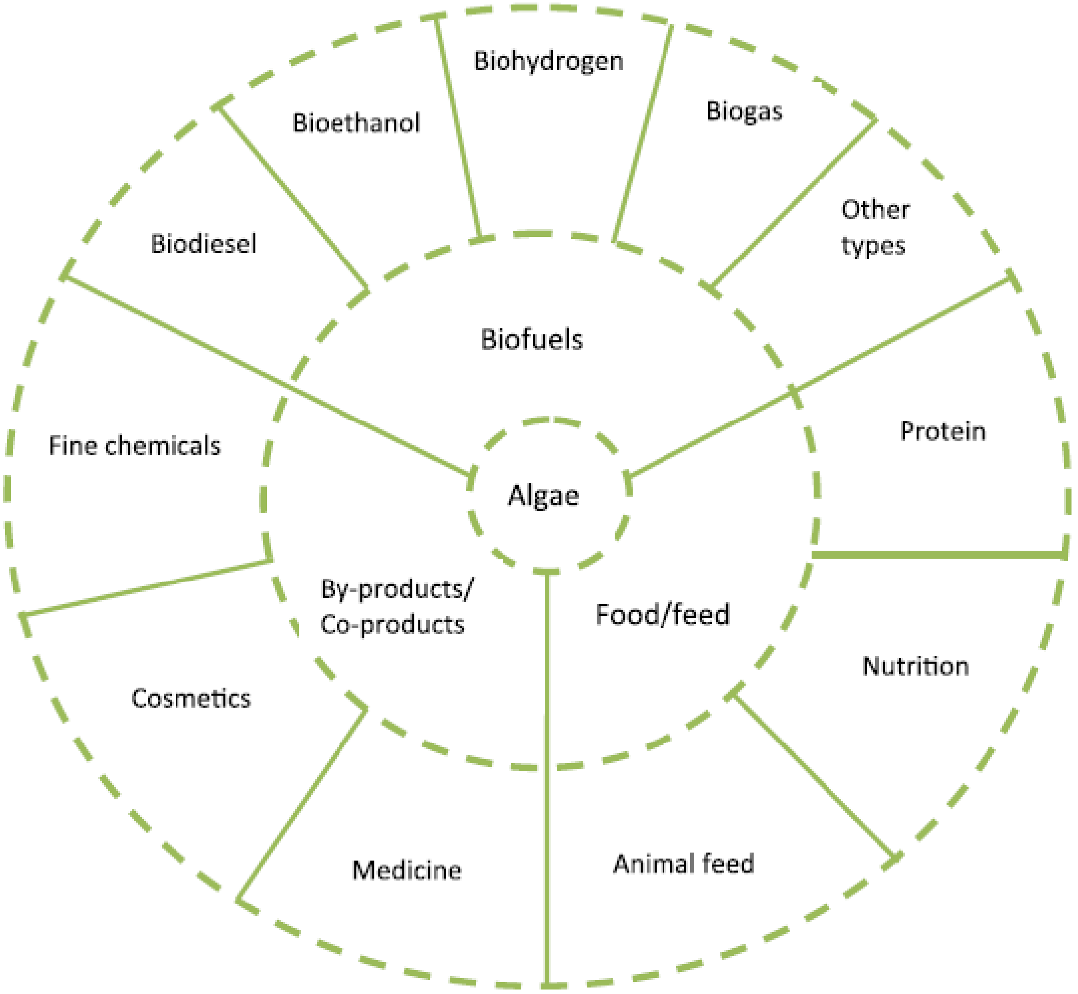

Figure 1 Potential products from microalgae during biorefinery

Source: *(Zhu, 2015)*.

Worldwide there are about 55 000 species and more than 100 000 strains of marine, brackish, fresh water and terrestrial algae. But over the world commercially cultivated are only a few species of algae. Major classification of algae is based on their photosynthetic pigmentation variations, namely green, blue-green, red, brown and golden algae (Vassilev, 2016). Algae are the fastest growing plant in the world and generally divided into macroalgae and microalgae based upon morphology. The macroalgae or “seaweeds” are larger, oceanic multicellular plants growing up to 60 m in length. Microalgae are microscopic, mostly existing as small cells and inhabitants of fresh, sea and even waste water systems (Sirajunnisa, 2016).

Although growing algae in open ponds has been done for decades, there is still a lot of research necessary in how to efficiently grow algae in large systems with a surface area per pond of 10 ha and greater and therefore produce biofuels economically. Especially the design of larger algae ponds remains a challenge since there is virtually no practical experience of the behaviour of these large ponds (Rarrek, 2016).

4.2.1. Macroalgae

Macroalgae also called seaweeds, constitute the most important organisms in marine ecosystems for the prevention of eutrophication and pollution (Sambusiti, 2015). Macroalgae are comparatively large, multicellular and photoautotrophic organisms which belong to the lower plants, consisting of leaf-like thallus instead of roots, stems and leaves. They are classified into three major groups according to the thallus colour derived from photosynthetic pigmentation: green (*Chlorophyta)*, red (*Rhodophyta)* and brown (*Phaeophyta)* (Vassilev, 2016).

The world amount of mass-cultivated macroalgae has continuously increased during the last ten years, reaching a total amount 16 × 10^6 wet metric tons in 2010. The pigment growth and chemical composition of macroalgae are significantly affected by their habitat conditions (light, temperature, salinity, nutrient, pollution) (Sambusiti, 2015). In terms of chemical composition, macroalgae, except green algae, do not have high content of starch and oil. They do not contain lignin, but have high contents of water (up to 90%) and minerals such as alkali metals. They contain low amount of proteins and lipids, but a high content of carbohydrates (Sambusiti, 2015; Vassiliev, 2016).

Carbohydrates of green, red and brown algae differ in quality and quantity, according to their species. Generally, the amount of carbohydrates varies between 30-60%, dry weigh. Green algae are mainly composed of mannan, ulvan, stratch and cellulose. The main polysaccharides of brown algae are alginate, laminarin, fucoidan, cellulose and mannitol. Red algae are mainly composed of carrageenan and agar as polysaccharides (Sambusiti, 2015).

4.2.2. Microalgae

Microalgae are one of the most primitive forms of plants. They are unicellular or simple-multicellular photosynthetic microorganisms and have size of only <400 µm and normally of 1-30 µm in diameter. According to estimates there is about 50 000 species of microalgae, but only few were used practically. Microalgae are categorized in a variety of classes, mainly distinguished by their pigmentation, life cycle and basic cellular structure. The most important classes of microalgae are: diatoms (*Bacillariophyceae*), *green* (*Chlorophyceae*), blue and blue-green cyanobacteria (*Cyanophyceae*), golden (*Chrysophyceae*) and red (*Rhodophyceae*) algae. Diatoms are main life form in phytoplankton and in all probability represent the largest group of biomass producers on Earth (Vassilev, 2016). Green algae are abundantly found in fresh water than in marine waters. The golden algae are similar to diatoms and produce oils and carbohydrates. Microalgae are efficient producers of lipids and other great metabolites that work by utilizing nutrients in the presence of solar energy. The algal species found suitable for biofuel research includes different species of *Chlorells* sp., *Dunaliella* sp., *Botryococcus braunii*, *Nannochloropsis* sp. and many others (Bharathiraja, 2015).

Microalgae present many of advantages over terrestrial plants for the production of renewable fuels and chemicals. Major among these is the fact that many species of algae exhibit high growth rates and can be grown on non-arable land using wastewater, thus avoiding undesirable competition with food crops for land and water resources (Santillan-Jimenez, 2016). Also it is well known that algae have greater capacity to generate and store carbon resources because they are more efficient CO_2 fixers. Microalgae are able to mitigate CO_2 from 10 to 50 times higher than terrestrial plants. Producing 1 tonne of algal biomass fixes 1.6-2 t of CO_2 because approximately half of the dry weight of algal biomass is carbon. So, algae have a huge potential to considerably contribute to greenhouse gasses emission reductions right at the very first stage of the feedstock production (Vassilev, 2016).

Algae like most of the other photosynthetic organisms use light energy to convert CO_2 into organic compounds. Microalgae are more photosynthetically efficient than higher plants. Under normal growing conditions, microalgae yield a caloric value of 18-

21 kJ/g/day. Algal growth and productivity are highly affected by the light path. However, the optimal CO_2 concentrations, nutrient sources and biofuel yields must be investigated for each strain of microalgae (Bahadar, 2013).

According to Suganya et al. (2016) there are many advantages of algae over the terrestrial plants such as:

- Algae is the most promising non-food source of biofuels;
- Algae has a simple cellular structure;
- Algae contain lipid-rich composition and produce 15-300 times more lipid than traditional crops;
- A rapid reproduction rate and high growth rate;
- Algae biofuel contains no sulphur, is non-toxic and highly biodegradable.

4.2.3. Composition of algae

Composition of algae is different from terrestrial biomass. Algae are photosynthetic organisms with simple growing requirements (light, sugars, CO_2, N, P and K) that produce habitually organic components such as proteins, carbohydrates, lipids, nucleic acid and other organics. Algae biomass in comparison with the terrestrial biomass normally has higher values of inorganic matter, proteins, lipids and nucleic acids (Vassilev, 2016). In terms of chemical composition, microalgae are mainly composed of carbohydrates, lipids, proteins and other valuable components (pigments, anti-oxidants, fatty acids and vitamins) (Sambusiti, 2015).

One of the main components in algae is the **carbohydrates** fraction, and some of the most productive algae contain large amounts of these saccharides. Their bulk contents in algae are highly variable (4-83%, mean 30%, organic basis). Macroalgae are commonly more enriched in carbohydrates compared to microalgae. Additionally, microalgae have high contents of starch, while macroalgae, except green algae, do not have such high concentrations. Algae contain various carbohydrates which are distinctively different from those of terrestrial plants. Normally, algae do not contain lignin or contain quite limited amount of this component. Lignin contents are lower in the aquatic biomass and particularly in marine algae as compared to the terrestrial ones

(Vassilev, 2016). Carbohydrates are highly favourable as sources of biologically active molecules, such as cosmetic additives, food ingredients and natural therapeutic agents (Chew, 2017).

Microalgae can accumulate a high percentage of **lipids**, in which the lipids usually account for approximately 30-50% of their total weight. The lipid content is dependent upon culture conditions, such as high carbon to nitrogen ratio (C/N) in culture medium or under stress conditions. In order to increase the lipid content, higher C/N ratio is needed in the microalgae cultivation. The earlier lipid accumulation will start when the earlier nitrogen source is exhausted due to the lower amounts of nitrogen in the fermentation broth. Stress conditions, such as nitrogen starvation, high temperature, pH shift and high salt concentration, are required to enhance lipid productivity (Chew, 2017).

Macroalgae, except green algae do not have high contents of lipids (up to 5%). Comparison, microalgae have greater concentrations of lipids than macroalgae (Vassilev, 2016). Lipids are broadly classified as neutral or polar. A neutral lipid has no overall polarity. It is located inside the cells in the form of triglycerides, mono- and diglycerides or free fatty acids. They are more soluble in non-polar solvents such as hexane and chloroform. Neutral lipids are energy storage products. They are the common algal substrate known for biodiesel synthesis. In contrast, polar lipids contain polar groups, such as choline, ethanolamine, serine, water, glycerol and phosphatidyglycerol in phospholipids (Salam, 2016).

For example, lipids production in *Chlorella emersonii* could be as high as 58-63% dry weight when grown with low nitrogen levels, and *Chlorella protothecoides* contained 55% lipid (dry weight) when grown heterotrophically with corn powder hydrolysate under nitrogen limitation. To increase the productivity of the diatom: *Nitzschia laevis* a continuous fed-batch process was developed. Glucose, tryptone, nitrates and yeast extract were considered as essential media components to increase productivity. The optimum ratio of 31:1 glucose: nitrate increased cell growth yield to 22.1 g/l, these conditions also increased eicosapentaenoic acid (EPA) production (Bahadar, 2013).

Proteins are contained in vegetable biomass (oilseed crops) and algae as in animal biomass. Algae are able to develop high contents of proteins within their cells depending on species (Vassilev, 2016). Microalgae composition could be 40-60% composed by proteins. Protein is one of the important products of microalgae biorefineries and can be used for human or animal nutrition (Chew, 2017). Protein's content in microalgae varies between only 7-15% (Sambusiti, 2015).

4.3. Algae cultivation

The mass microalgae production was started in the early 1950s in Japan (Kumar, 2015). Literature offers a lot of models describing the growth of algae ranging from a very simple approach where the algae growth is only depending on a few parameters to very sophisticated models that even cover the complex processes which take place within the algae (Rarrek, 2016). Besides to natural environments, microalgae can be cultivated in freshwater, seawater and waste water open pond systems and closed photobioreactors (Vassilev, 2016). For the biomass, commercial production from algae are used open ponds and closed photobioreactors. Both have their advantages and disadvantages (Kumar, 2015). Open cultures are primarily located outdoors and rely on direct sunlight, while closed photobioreactors can be either indoors or, preferably, outdoors to use sunlight. One of the many advantages of closed photobioreactors is that most species can be grown there while open systems are more limited (Bahadar, 2013).

4.3.1. Open systems

Altogether, there are four major open systems: shallow big ponds, tanks, circular ponds and raceways ponds (RWPs). The choice of the open pond cultivation system depends upon types of algal species, local climatic conditions as are rainfall, solar radiation, local temperature, land slope and the cost of lands and water. For example, the location having rainfall less than 1 m per year was considered as desirable for constructing open ponds. Also in many countries, the operation of raceway ponds is not possible throughout the year, because of winter season. In winter, solar radiation and temperature drop to unacceptable level for the growth of microalgae (Kumar, 2015). Shallow big ponds and tanks are rarely used to cultivation of algae; those systems are very similar to natural systems. There is no control of contamination and growth of algae. Yield of biomass is less than in the other cultivation open systems (Hewes, 2015). In researches it was discovered that raceway ponds are the most promising cultivation open system. Compared with **circular ponds** RWPs has marginally higher biomass content as shown in Figure 2 and higher number of desired substance at the same outdoor conditions. Circular ponds are also more difficult to operating. For example, the cultures must be mixed manually every day (Rao, 2012). Today is nearly 95% of the total worldwide algal production based on raceway ponds systems (Kumar, 2015).

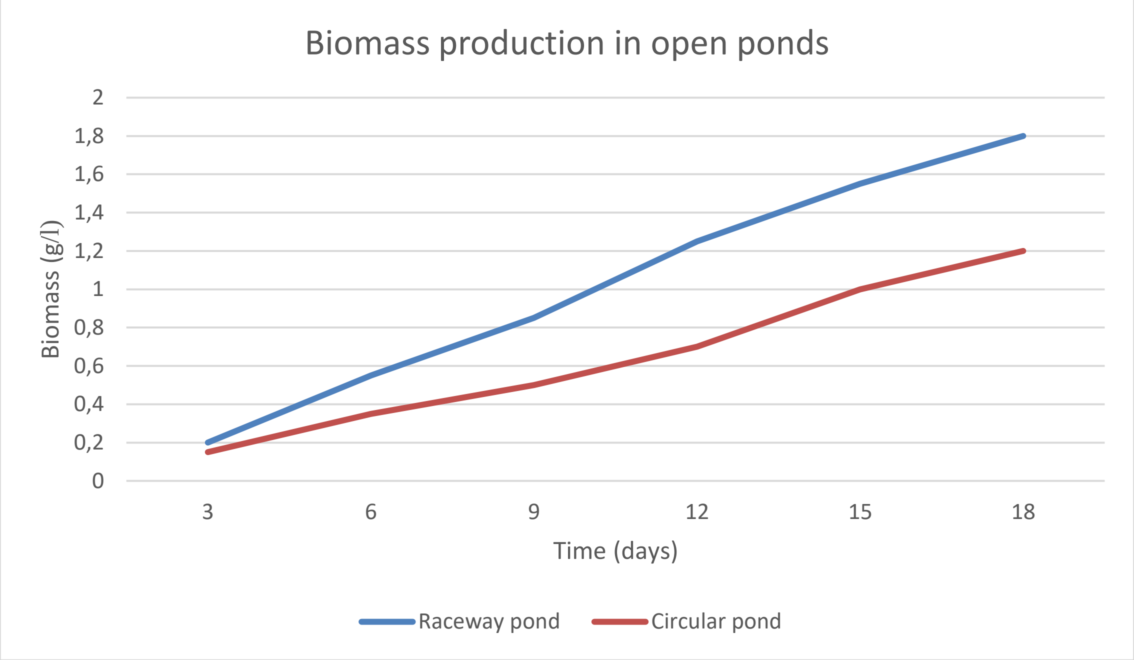

Figure 2 Compared algae biomass production in raceway and circular ponds

Source: *(Rao, 2012)*

Raceway pond was found to be better compared to circular pond (and other open systems). RWPs use the simplest form of algal cultivation (Kumar, 2015). Raceway ponds as shown in Figure 3 3 form closed circuits approximately 0.25 m wide and 0.4 m deep through which the water is circulated by a paddle wheel. They are shallow to maximize light penetration (Bahadar, 2013). Huge advantage is cost of production. Average lipid production cost in open pond ($12.73 per gallon) is significantly lower compared to that of photobioreactors ($31.61 per gallon). Also, the cost of commercial photobioreactors is more than 100 times higher than open ponds (Kumar, 2015).

Raceways are extremely cost effective to construct and operate, but also easy to clean. There are low energy inputs needed and easy maintenance. Whole system is simple (Milano, 2016). Also in a question of global warming potential, algal based biodiesel obtained from RWPs is nearly 80% lower than the fossil-derived diesel (Kumar, 2015).

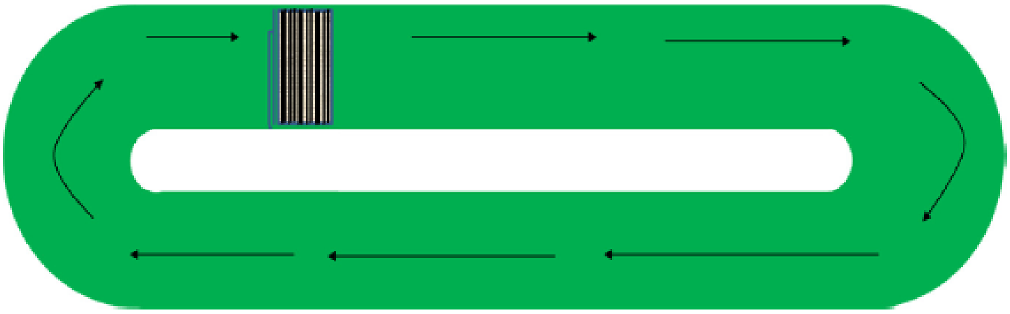

Figure 3. Schematic diagram of paddle-wheel driven raceway pond

Source: (Kumar, *2015)*.

Unfortunately, raceway ponds are intended to cultivate selected microalgae growing only in specific environments. Some of microalgae generally cultivated in raceway ponds are *Nannochloropsis* sp., *Chlorella* sp., *Tetraselmis* sp., *Arthrospira platensis, Dunaliella salina* etc. (Kumar, 2015). Open ponds have lower productivity per unit area and volume than closed photobioreactor systems because of the low light-to-volume ratio. There is also problem that these systems can be easily contaminated by other microorganisms that can compete with the cultivated algal strain. That is the limitation, sometimes cited as a serious limitation of open systems (Bahadar, 2013). In raceway ponds, there is no control over the production of biomass and harvesting cost are relatively higher (Milano, 2016).

4.3.2. Closed photobioreactors

Closed photobioreactors are designed to overcome and beat the limitations of open pond systems. There are many types, as tubular, flat plate, column and biofilm photobioreactors. They can be airlift, flat inclined, bubble column, column aeration, solar penthouse-roof and multistage continuous flow photobioreactors (Bahadar, 2013). Photobioreactors (PBRs) have significantly higher volumetric algal productivities (0.2-3.8 g/l/day) compared to those of raceway ponds (0.12-0.48 g/l/day). Closed photobioreactors prolong the gas retention time and improve the mass transfer efficiency. Closed PBRs also offer greater control over the whole process parameters. PBRs can be used to cultivate a greater range of algal species than open systems (Kumar, 2015).

Tubular photobioreactors are the most widely used and considered the most promising, because they yield high biomass and have short harvest times. In Figure 44 it is shown that they are composed of parallel tubes (0.2 m in diameter or less) and are positioned horizontally or vertically to maximize sun exposure (Bahadar, 2013). Algal culture is circulated in those transparent tubes by a centrifugal pump and intermittently passes through a degasser – an air-sparged vessel where the accumulated oxygen is blown off. High oxygen concentrations reduce the algal productivity and optimizing the degassing is an important feature of the design process (Norsker, 2011). Tubular PBR can also be designed helically to provide a larger surface area to volume ratio. This design maximizes light penetration, limits contamination, allows for easy temperature control and provides maximum CO_2 transfer in the culture medium (Bahadar, 2013).

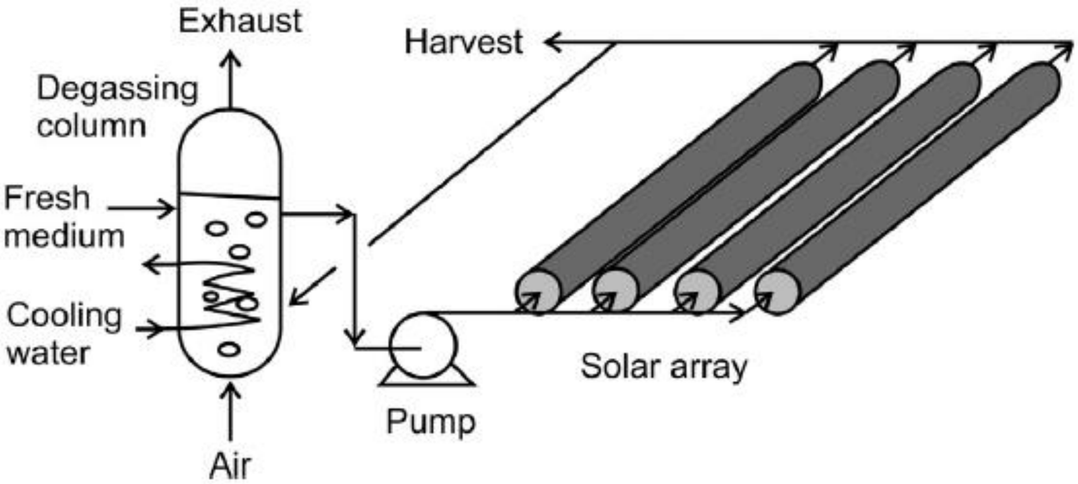

Figure 4 Working scheme of a horizontal tubular photobioreactor

Source: *(Bahadar, 2013)*.

Airlift photobioreactors are simple and cost-effective reactors for the mass culture of various types of algae. They are made of acrylic glass, which is inexpensive and easily obtained and meet the desired criteria for new generation photobioreactors of high light penetrations and biomass production, ease of maintenance and minimal contamination (Bahadar, 2013). The main advantage of the airlift photobioreactor was its easy construction from material available on the market at very low cost. Airlift reactor fulfilled the main requirements claimed to be essential for the design and development of a new generation of photobioreactors. The low-cost reactor, may be useful for mass production of microalgae in developing countries (Xu, 2002).

Biofilm photobioreactor offers a concentrated amount of algal biomass compared to others ways. The system also reduces the energy and water requirements of cultivation. Main parts of the system are the biofilm growth surface, a nutrient medium recirculation system and an illumination system as shown in Figure 55. The system is open for further improvement through research on thermal management, mass and light transfer optimization as well as algal species selection (Ozkan, 2012).

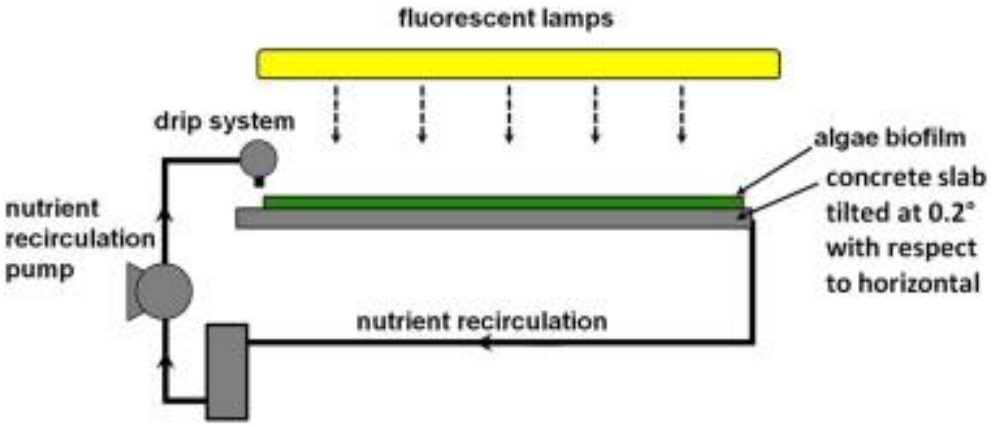

Figure 5 Scheme of the algae biofilm photobioreactor system

Source: *(Ozkan, 2012)*.

However, closed PBRs are much more expensive to construct than open systems (Bahadar, 2013). Also, the operation and cleaning of thousands of individual PBRs are laborious, costly and time consuming. The water and energy consumption, total actual area occupied by the PBRs, and also the problem of long term resistance to contamination are other disadvantages of photobioreactors (Kumar, 2015).

4.4. Energy products from algae

Algae can be used to produce many kinds of bio-products during the biorefinery, depending on the microalgal compositions. The extracted lipids from microalgal cells can be mainly converted into biodiesel, whereas the carbohydrates, including the starch and cellulose, can be transferred to bioethanol through fermentation. Carbohydrates, proteins and fats in microalgae tissues can be converted into methane and biohydrogen via anaerobic digestion. Except biodiesel, bioethanol, biogas and biohydrogen, microalgae can also be converted into biobutanol, bio-oil, syngas, jet fuel, etc. via thermochemical, chemical and biochemical conversion processes (Zhu, 2015).

4.4.1. Biodiesel

Biodiesel can be derived from edible oil seed crops such as sunflower, palm, rapeseed, soybean, etc. which are considered as first generation feedstock. Those feedstocks are unsustainable. Second generation has importance in last few years (jatropha, karanja, cooking oil, animal fats), but second generation feedstocks are not sufficient to entirely substitute the present transportation needs. Recent focus is on microalgae as the third and fourth generation of feedstock (Nautiyal, 2014). For example, Figure 66 shows a comparable biodiesel yield per hectare of farmland for different crops, where algae are the most promising feedstock. While the yields of most common vegetable oils are below 5 000 litres per hectare, the yield from algae as a feedstock reaches 50 000 l/ha/year, indicating tremendously a much higher prospect (Galadima, 2014).

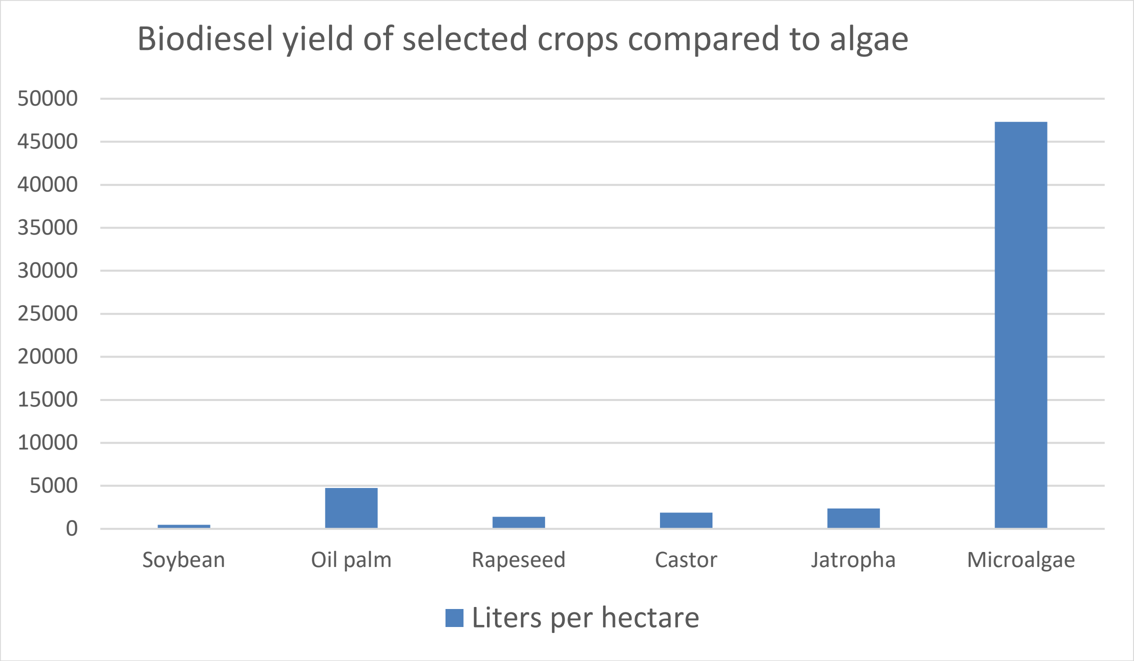

Figure 6 Yield of biodiesel per hectare for some crops compared to algae

Source: (Galadima, *2014)*.

Microalgal biodiesel has the potential to meet the global demand for transportation fuel, but this technology still needs to overcome many hurdles, before being deployed at large scale and becoming competitive in the fuel market. The main challenge is to achieve sufficient outlay for a commercial production of microalgal biodiesel. Based on estimated costs for 2009, one barrel of microalgal oil-based biofuels would cost $300-$2600 to produce using the current technologies, while one barrel of crude petroleum costs $40-$120. Cost reduction is very important in oil rich biomass production for cost effective microalgal biodiesel production. Therefore, improvements are necessary to overcome several obstacles facing upstream and downstream processes. These include finding favourable strains, optimizing culture conditions, improving biomass production procedures, and oil extraction techniques (Taleb, 2016).

4.4.1.1. Biodiesel production

The technical process of algal biodiesel production includes several different technology components: algal growth, algae dewatering, oil extraction, oil esterification, and a process for the conversion of the oil-extracted algae (Brownbridge, 2014). Those processes of cultivation, oil extraction and final conversion into biodiesel are basically comparable to those of other edible crops such as soy, sunflower and palm. These facts could be attributed to important factors leading to the escalated growth-rates for the algae species around many places in the world (Galadima, 2014).

Suitable algae growth systems for biodiesel production are both: open raceways and photobioreactors. Generally, it depends on decision which to use. The algae lipid content usually increases if cultivated under nitrogen-deficient conditions. However, the inverse relationship between the lipid content and the annual productivity somewhat offset the total amount of oil produced annually. The required carbon for algae growth can be provided by bubbling flue gas from external sources into the growth medium, or alternatively via utilisation of waste water. In the latter case, the treated water should be also considered as a product beside the produced biodiesel, as in this case the algae production essentially eliminates the need for the treatment of the wastewater. A major challenge is to increase concentration of the feedstock. Default concentration is between 0.05 wt% and 2 wt%. The initial feedstock can be effectively concentrated up to nearly 10 wt% using physical precipitation methods with low energy demands (Brownbridge, 2014).

Harvesting of microalgae is the principal step in the overall process of biofuel production because of their diminutive size (3-30 µm). One of the difficulties in large scale production of microalgae is the development of efficient technique to separate cells, maintain their viability and bioactivity prior to use in the field. The harvesting step accounts almost 20-30% of the total cost in the microalgal biodiesel production. In order to remove large amount of water for separating microalgae, a suitable harvesting method may have achieved by physical, chemical and biological ways. There are harvesting methods for separating microalgae as centrifugation, gravity sedimentation, filtration, electrolytic method, bioflocculation and magnetic nanoparticle separation. Each of them has its advantages and disadvantages (Sirajunnisa, 2016).

Anyway, due to small particle sizes and water-like density, further dewatering and drying of the microalgae slurries is significantly energy and carbon intensive. Therefore, it is likely that the technologies that directly fractionate and convert dilute microalgae slurry can offer inherent advantages over the conventional processes such as oil extraction from dried feedstock (Brownbridge, 2014). Oil extraction is basically the initial and critical step in biodiesel production from plants after harvesting. An attractive procedure is one that ensures reduced extraction cost but high oil yield. The two fundamental methods available for algae today are the mechanical and chemical methods. The mechanical method is mainly expeller press or ultrasound-assisted whereas hexane solvent, soxhlet and supercritical fluid extraction are the available chemical methods. The mechanical method requires algae drying, thus making it energy intensive on the other hand health and safety issues are critical for the chemical option. Adopting supercritical extraction process involved the use of expensive high pressure equipment that is also energy intensive (Galadima, 2014).

After extraction, the algae oil can be converted into biodiesel at high yields via transesterification process. To increase usability in algal production, there are three scenarios plausible with respect to the conversion of the oil-extracted algae in a biofuel-only algae conversion strategy. Each of which can prove more viable depending on the upstream harvesting and oil extraction processes and several other factors: 1) they can be combusted in boilers to generate process heat and electricity, 2) they can be converted to biogas using anaerobic digestion, and 3) they can by gasified to produce syngas, which can subsequently under go the Fischer-Tropsch process to produce more diesel fuel, or burnt in gas turbines to generate electricity (Brownbridge, 2014).

4.4.2. Bioethanol

Bioethanol production is not a new concept. It was initiated during fuel crisis over the world in 1970s and the capacity of ethanol production grew from about one billion liter in 1975 to more than 39 billion litters in 2006 and reached 100 billion litters in 2015. As all biofuels, also bioethanol production is categorized into first, second and third generations based on various feedstocks, production technology and their level of development. Algae could be a potential alternative to current biofuel crops such as corn as they do not require agricultural land (Sirajunnisa, 2016). Biomass production of algae is 5-10 times greater than for land-based terrestrials due to more photosynthetic efficiencies. The algae do not contain lignin, which is a physical obstacle to enzymatic hydrolysis and cannot be removed by pretreatment. This character of algae is beneficial in the pretreatment and enzymatic hydrolysis of bioethanol production process (Bibi, 2016). However, very little research has been done on production of bioethanol from algae and now it is being concentrated by many scientists over the world due to its more significance than the terrestrial crops (Sirajunnisa, 2016).

Bioethanol fuel reduces lead, sulfur, CO and particulate emissions. Ethanol as a fuel in Brazil reduced carbon emissions, resulting to a reduction of 15% of Brazil´s total emissions. Bioethanol fermentation from microalgae requires less energy than biodiesel production. The unsolicited CO_2 byproduct can be recycled to cultivate additional algae. Main species of microalgae for ethanol production are *Chlorella vulgaris* and *Chlorococcum spirulina* (Bahadar, 2013).

Macroalgae are also good feedstock for bioethanol. Those algae or “seaweeds” are multicellular plants in marine ecosystem, growing rapidly and can sizes, as it was mentioned above, up to 60 m in length. The most important for biofuel like bioethanol production are three broad groups based on their pigmentation: brown seaweed, red seaweed and green seaweed. Macroalgae is referred as ideal candidate for bioethanol production than the microalgae because they don´t contain high amount of lipid as microalgae, instead they have high content of natural sugars and other carbohydrates, which can be fermented to produce alcohol-based fuels (Sirajunnisa, 2016).

From three major groups is brown seaweed one of the promising biomass for biofuel production because cultivation productivity based on area is the highest among three types of macroalgae; approximately 40 kg wet biomass/m^2 of gulf-weed (*Sargassum muticum*), compared to 2.3 and 6.6 kg/m^2 of green laver (*Ulva lactuca*) and agar weed (*Gelidium amansii*). The large-scale cultivation of brown algae is already practiced in several countries including Korea, China and Japan. Compared to microalgae, brown algae have more sugar and less oil contents, almost 55% of the dry biomass. Therefore, brown algae are a more suitable feedstock for bioethanol production than biodiesel. It was claimed that bioethanol productivity from macroalgae per hectare per year could theoretically be two times higher than sugarcane and five times higher than corn. Roughly 70 million dry tons of macroalgae are cultivated and harvested over the world in offshore and near-shore coastal farms. However, this production is mostly for food production (Lee, 2016).

4.4.2.1. Bioethanol production

Cultivation of microalgae is the same as in production of biodiesel there are two ways as open ponds and closed photobioreactors. On the other hand, there are macroalgae “seaweeds” which are cultivated in marine ecosystems. Cultivation of seaweed is easy and can be harvested by simple methods, while seaweed can be directly cultivated in open sea, microalgae had to be cultivated in a controlled, designed system. Generally, a part of the current seaweed production comes from harvesting natural population or collecting beach-cast seaweed. Growing macroalgae in a dedicated cultivation system is worth considering. For seaweed cultivation, several important factors such as temperature, nutrient and light source must be analysed with other functions of the sea, distance from shore as they imply energy and time spend on transportation. Usually, seaweeds are cultivated in lagoons or sheltered bays so it attains nutrients directly from the seawater. Several methods are routinely applied for cultivation and harvesting of seaweeds such as fixed off-bottom, longlines and rock-based farming (Sirajunnisa, 2016).

Bioethanol can be fermented from all kind of macroalgae by converting their polysaccharides to simple sugars and by employing appropriate microorganisms. Since macroalgae have various carbohydrates such as starch, cellulose, laminarin, mannitol and agar, carbohydrate conversion to sugars and the choice of appropriate microorganisms are pivotal for successful bioethanol fermentation. Also some microalgae are used for ethanol production like *Cholorococcum*, *Chlamydomonas* and *Chlorella*. Fermentative ethanol production from microalgae like *Chlorococcum* and *Chlorella vulgaris* result in better conversion rates than that of another species (Trivedi, 2015).

The most promising macroalgae to produce bioethanol is brown algae, there is no lignin and thereby no extensive pretreatment is used to release sugars, but just using simple operations such as milling or crushing. There is no moral issue associated with the use of brown algae for biofuel production. Cultured brown algae are harvested by both manual and mechanical methods. The harvested algae are than normally treated with milling to reduce biomass sizes for efficient saccharification or alginate extraction. The saccharfied broth can be used for bioethanol fermentation. The most abundant sugars in brown algae are alginate, mannitol and laminarin. Mannitol and glucose are normal sugars that are efficiently used for bioethanol fermentation. Laminarin and mannitol from *Laminaria hyperborea* extracts were fermented to bioethanol under oxygen-limiting conditions using *Zimobacter palmae*. Alginate is a structural polysaccharide in the cell wall of brown algae. In some brown algae, alginate constitutes up to 60% of the total sugars. Thereby, alginate, the most abundant carbohydrate, should be utilized for the production of bioethanol (Lee, 2016).

4.4.3. Other biofuels

Biomethanol is possible product of microalgae biomass, although bioethanol has more attention, because biomethanol is corrosive, toxic, and has a high cold point, which causes engine start problems in cold weather. *Spirulina* is converted into methanol by gasification (Bahadar, 2013).

Biogas is another possible biofuel from algae biomass via fermentation. The main component of biogas is methane. Algae biomass is great source of polysaccharides and lipid substances (Dębowski, 2013). According to Quinn (2014) it is very important to decide if we remove energy rich lipids to biodiesel production and use the rest of biomass to produce methanol. Or we use whole biomass to anaerobic digestion to produce biomethane. Production of methanol in way of removing energy rich lipids for fuel production dramatically decreases the methane yield. It is worth considering if the economic value is prosperous.

Biohydrogen production is of an increasing interest as fossil fuel supplies are being depleted. A number of methods can generate renewable hydrogen, such as biomass gasification, electrolysis, and photovoltaic generation, which all produce hydrogen for less than $20/GJ, which is quite reasonable (Bahadar, 2013). The carbohydrate content in a substrate is considered as a key indicator for suitability for fermentative hydrogen production. A high carbohydrate is connected with high theoretical hydrogen production potential. Algae-based fermentative hydrogen would be very beneficial for renewable transport fuel production in coastal zones. Fermentation is proposed as a first step for the algae-based biorefinery (Xia, 2016).

One of the biggest challenges in front of the airline industry is the increase in air travel demands. The airline industry consumes over 5 million barrels of oil per day all over the world. The energy intensity in terms of Btu per passenger is lowest for railways followed by airlines. Upon combustion, the aircraft jet fuel produces carbon dioxide, water vapour, nitrogen oxides, carbon monoxide unburned or partitally combusted hydrocarbons, particulates and other trace compounds (Trivedi, 2015).

Renewable **jet fuel** for the aviation industry, also termed bio-jet fuels could reduce flight-related greenhouse-gas emissions by 60-80% compared to fossil fuel based jet fuel. The oil of microalgae can be converted into jet fuel by hydrotreatment. Algae oil is specially modified to contain the same types of molecules that are typically found in conventional petroleum-based jet fuel. The other method to produce jet fuel is through Fischer-Tropsch process. F-T fuels are high quality fuels and can be derived from biomass (microalgae). As safety is paramount issue in aviation fueling, very specific needs and requirements have to be met. Currently, plenty of research is going-on to produce biofuel from microalgae source, in companies of global importance such as Shell and UOP (Trivedi, 2015).

4.5. Non-energy products from algae

Production of high value byproducts from macroalgae and microalgae and their commercial application can provide a promising opportunity to commercialize microalgal biofuels. Algae as a potential renewable resource is not only used for biofuels but also for human health, animal and aquatic nutrition, environmental applications such as CO_2 mitigation, wastewater treatment, biofertilizer, high-value compounds, synthesis of pigments and stable isotope biochemical (Suganya, 2016).

Algal polysaccharides represent a class of high-value compounds with many downstream applications in food, cosmetics, textiles, stabilizers, emulsifiers, lubricants and clinical drugs. Algal sulphated polysaccharide exhibits a wide range of pharmacological activity, including acting as antioxidant, antitumor, anticoagulant, antiviral and immunomodulating agents (Trivedi, 2015).

Algae contain a multitude of **pigments** associated with light incidence. Besides chlorophyll, the most relevant are phycobiliproteins, which are helpful in improving the efficiency of light energy utilization and carotenoids which serve as photo-protectors against the photo-oxidative damage resulting from excess energy captured by light-harvesting antenna. Ketocarotenoid, known for its powerful antioxidant properties is also obtained in algae. Other algal pigments are used for chicken skin coloration (lutein, zeaxanthin and canthaxantin) or being used for food and cosmetics applications (phycobiliproteins, phycocyanin and phycoerethrin). Carotene is currently used in health foods as a vitamin A precursor and also for its anti-oxidant effects. Many pigments from algae can also be used as natural food colorants, for instance, in orange juice, chewing gum, ice sorbets, candies, soft drinks and dairy products (Trivedi, 2015).

5. Conclusion

In last decades, expansion in exploring biofuels from algae has marginally growth as a renewable energy from both microalgae and macroalgae has showed a great potential.

Cultivation of algae made a huge progress in last decades but still both cultivation ways need to cross over many obstacles. It must be more effective technologies to grow quantity and, also quality. On the other hand, there should be effective commercialization to visualize algae and algae products such as biofuels and non-energetic by products.

The most promising cultivation technology from open systems is raceway ponds, mainly because it is relatively cheap, there are low energy inputs and it is easy to clean and maintenance it. On the other hand, raceway pond and all other open pond technologies have poor biomass productivity, require large area of land and cultures are easily contaminated. Other cultivation systems such as photobioreactors are more sophisticated technologies. The most promising seems to be tubular and flat plate photobioreactors due to high biomass productivities, large illumination surface area and good light path. But those technologies also demands large land space, have difficult scale-up and in comparison with open systems are more expensive in primary costs and, also in maintenance.

Biodiesel and bioethanol from algae bring huge progress in biofuel production. Algae biomass as the only can offers total compensation for fossil fuels. Advantages of biodiesel from algae oil are rapid growth rates almost anywhere; a high per-acre yield (7-30 times greater than the following best energy crop – oil palm). Certain species of algae can be harvested daily. Algae biofuel is non-toxic, contains no sulphur and is highly bio-degradable. Disadvantages are that biodiesel from algae incorporates many polyunsaturates and it is relatively new and expensive production technology.

Biodiesel has a significant potential; however high cost and limited supply of renewable oils prevents it from becoming a serious competitor for petroleum fuels. Cost of producing microalgal biodiesel and also bioethanol can be reduced substantially by using a biorefinery based production strategy, improving capabilities of microalgae through genetic engineering and advances in manufacturing of photobioreactors. Same as a petroleum refinery, a biorefinery uses every component of the biomass raw material to produce useable products. Co-products and byproducts of algae biofuels may be the potential future for economic growth.

To conclude, among major advantages of algae belong high productivity with rapid growth rate and high growing yield. Algae are non-food source of biofuels and can be grown on polluted water. Algae represent sustainable, renewable, effective and environment friendly biofuel source.

On the other hand, there are not established efficient appropriate technologies for growing, harvesting, transport, storage and pretreatment, for these reasons is the whole process challenging economic; and only biofuel production approach is not commercially viable.

Due to disadvantages of only algae-based biofuels production it is necessary to conduct biofuels production in cooperation with non-energetic industries such as cosmetics, food production, textile and pharmaceutical which have a great economical potential.

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