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Microalgal Biorefinery Applications

Ebru Işık[1], Ebru Akkaya[2]

Abstract

This study aims to point out the potential of microalgae applications with biorefinery approach. Microalgae applications allows us to produce energy products, nonenergy products such as carbonhydrates, pigments, and proteins and other high value products while we treat wastewater. The biorefinery approach is the best alternative for fossil-based refineries, so far. Commonly biorefineries use corn, sugar crops, grasses, starch crops, palm oil, and also microalgal biomass as a feedstock [1]. Microalgal biorefineries stand out among other biorefineries with a broad commercial spectrum of products, less land requirement, the potential of harvesting in all seasons and short biomass harvesting time. Besides all these advantages, microalgae provide bioremediation of heavy metals and nutrient removal from polluted and wastewater, CO_2 mitigation, and O_2 production via photosynthetic growth.

Keywords: Microalgae applications, biorefinery, circular economy

1. INTRODUCTION

The world population is increasing dramatically. The energy need per capita and the daily water and food demands are increasing in tandem. The average person's carbon footprint is constantly increasing. Day by day, our demands from nature are both diversifying and increasing in quantity. Resources are rapidly becoming polluted and depleted due to unconscious consumption, and these resources are no longer accessible to most people. In the circumstances, it has become more difficult than ever to live in healthy and equal conditions. Therefore, it is important to develop a sustainable and environmentally friendly industry. At this point, less water consumption, minimizing wastewater discharge, implementation of clean production plans, systematic waste management, reduction of emissions and environmental, economic and social sustainability of production gain importance for industrial organizations. The biggest challenge for environmentally friendly industries is to find renewable sources to meet their energy demands.

Due to the exponential growth of the human population, global urbanization and industrialization have increased, which can promote high energy consumption. Today, fossil fuels are the world's primary energy source and will remain the world's leading power source. (Figure.1) Fossil fuels are projected to meet about 84% of global energy demand by 2030[2]. Coal, oil and natural gas account for 81% of the country's total energy consumption [3]. This energy is used to heat and power homes, businesses, run automobiles and power manufacturing. Nearly three-fourths of the emissions caused by human activity in the past 20 years were also brought on by fossil fuels.

[1] *Corresponding author: Yildiz Technical University Environmental Engineering Department, 34220, Esenler/İstanbul* *ebru.isik@yildiz.edu.tr*

[2] *Yildiz Technical University Environmental Engineering Department, 34220, Esenler/İstanbul* *ekoca@yildiz.edu.tr*

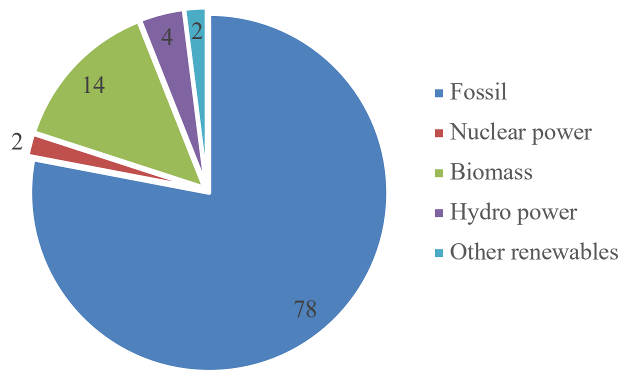

Figure 1. Shares of biomass in total energy consumption worldwide in 2015[4]

In addition to providing for our energy requirements, burning oil, coal, and gas contributes to the current global warming crisis. Burning fossil fuels results in significant carbon dioxide production. Climate change is caused by carbon emissions, which trap heat in the atmosphere. When burned, fossil fuels release more than just carbon dioxide. 35 percent of the harmful mercury emissions in the United States, as well as two-thirds of the sulfur dioxide emissions in the country (which contribute to acid rain), and the great majority of the particulate matter in our air, are produced only by coal-fired power plants. [5]

Harmful air pollutants are released by fossil fuels long before they are consumed. Every day, 17.6 million Americans are exposed to harmful air pollution caused by running oil and gas wells, transportation hubs, and processing plants. [5] These include substances known to cause cancer, such benzene and formaldehyde. In addition to all these environmental impacts, fossil fuels have also been found to cause land degradation, water pollution and acidification of the oceans. Therefore, now, engineers and scientists are exploring for ways to lessen our reliance on fossil fuels while also improving the environmental benefits of using these fuels.

Because of all these environmental concerns, refineries are replaced by plant-based biorefineries. Crops with high biodiesel and biogas potential such as corn, sugar beet, etc. were processed in biorefineries to produce biodiesel, biogas, bioethanol, biojetfuel. While the biorefinery approach offers us the possibility of sustainable processing, the use of edible plants as raw materials is in conflict with the world's food supply. In order not to jeopardize access to water and food for future generations, developed countries have regulations on the use of edible plants in biorefineries. Thus, algal biorefineries become a better option for biorefineries.

Algae biorefineries are economically viable, renewable and carbon-neutral plants. They are more efficient, environmentally compatible and socially acceptable. Along with environmentally friendly energy products, microalgal biorefineries enable the production of various pharmaceuticals, cosmetics, feed and food products and other valuable chemicals. Above all, algal biorefinery facilities fit into the circular bioeconomy. The term circular bioeconomy is an integrated concept of circular economy and bioeconomy. Algal biorefineries can be said to have a circular economy due to their improved resource and environmental sensitivity, lower greenhouse gas footprint, reduced dependence on fossil resources, and utilization of by-products and waste materials from multiple sources. In addition, compared to conventional diesel, algal biodiesel emits less particulate matter, sulfur oxides (SO_x), nitrogen oxides (NO_x) and organic air pollutants [6].

2. BIOREFINERY CONCEPT

In the 1990s, the term "biorefinery" emerged in reaction to industrial trends [7]. First, there was a rise in industrial understanding of the necessity of using biomass resources more sanely from an economic and environmental standpoint. Then, refineries started to utilize different biomasses instead of fossil resources. The fundamental technologies between biological raw materials, industrial intermediates, and final products are combined in biorefineries.

In order to understand what biorefineries are and what they aim to achieve and what their scope is, it is necessary to take a closer look at the definition of a biorefinery. As seen below, several definitions exist in literature.

- "Biorefining is the sustainable processing of biomass into a spectrum of marketable products and energy." [8], [9].

- "Full utilization of the incoming biomass and other raw materials for simultaneous and economically optimized production of fibers, chemicals, and energy." [7].
- "Maximizing the economic value from plants which requires an improved business model and corporate transformation." [10].
- "Facilities that can combine biomass conversion processes and equipment to generate fuels, power and new materials in an economically, socially and environmentally sustainable way." [7].
- "Biorefinery is a facility that converts biomass into a broad range of products for various markets (food, feed, materials, energy) and which is characterized by low energy demand through high process integration and low waste production as well as a high flexibility towards changing markets for raw materials and products." [4].
- The integration of different conversion processes to produce energy and value-added chemicals into a single facility is called a biorefinery.

Based on the definitions, it can be said that biorefineries can create a business model that can integrate traditional industries with different refineries, realize a circular economy, and ensure sustainability with less waste, more efficient production and in a more environmentally friendly way. Biorefineries can be classified into four different categories: biosyngas-based refineries, pyrolysis-based refineries, hydrothermal upgrading-based refineries, and fermentation-based refineries [8]. Biofuel sources are classified based on four feedstock generations: edible food crops (first generation), lignocellulose-based (second generation), algae (third generation), and genetically modified plants and microorganisms (fourth generation) [6].

Biorefinery has a process scheme consisting of 2 stages. The first stage can be called primary refinery or upstream processes. The second stage can be called secondary refinery or downstream processes. Primary refinery the section of a biorefinery where the biomass is either fractionated into its primary components or transformed into products with higher energy densities. Secondary refinery a biorefinery's section where the primary refinery's output is transformed into final products [4].

3. MICROALGAE

The term microalga (microalgae:plural form) is derived from the words micro- and alga, meaning "small". Phytoplankton and microphytes are synonyms [11]. Microalgae are microscopic, single-celled and mostly photosynthetic organisms. Although they are unicellular, some can live in colonies. Their ability to photosynthesize is due to the presence of photosynthetic pigments. They are colored and named according to the dominant pigment type, such as green algae, red algae, or brown algae. Those that lack photosynthetic pigments grow as heterotrophs and feed on other organisms. Some species grow as mixotrophs, meaning that they can both photosynthesize and feed on other organisms.

Microalgae have between 200,000 and 800,000 species, of which 50,000 have been described [12],[13]. These organisms can convert solar energy into a variety of biomolecules, including carbohydrates, proteins, lipids and triglycerides. Microalgae can grow in a variety of habitats, including freshwater, saline water, terrestrial, symbiotic, and synthetic ecosystems (fountains, pools, bottles,plant pots).

Microalgae have the ability to remove carbon dioxide from a variety of sources, including atmospheric CO_2, industrial exhaust gases (such as flue gas and flare gas), and fixed CO_2 in the form of soluble carbonates [8]. Some are also capable of fixing nitrogen [11]. They can remove wastewater of heavy metals, uranium, and other pollutants and degrade organic compounds including carcinogenic polyaromatic hydrocarbons.

Since algae are an important source of carbon absorption and consume atmospheric nitrogen oxides, another well-known hazardous greenhouse gas, large-scale algal development is beneficial to the environment. Additionally, algae are a key source of biofuels and produce at least 50% of the planet's photosynthetic biomass [12].

Research on the use of algae for bioremediation of wastewater dates back to the 1950s [8]. There are many types of wastewaters that can be bioremediated by growing microalgae, nutrient-rich wastewaters with high N, P and C content can be used for different target crops. Suitable wastewaters for growing microalgae are listed below.

- Municipal wastewater [14]
- Dairy industry wastewater [15]
- Poultry industry wastewater
- Piggery wastewater [15]
- Paper and pulp industry wastewater
- Beer and wine industry wastewater [15]
- Starch and juice industry wastewater [16]
- Agricultural wastewater [14], [17]

- Textile industry wastewater [15], [18]
- Palm oil mill effluent [18]
- Rubber wastewater [18]
- Soybean processing wastewater [15]
- Aquaculture wastewater [15]

Microalgae have become a popular research topic in recent years. Because the product range is very wide and the usage areas are very high. Microalgae products and their applications are briefly as follows;

Energy products from algae;

- Biodiesel
- Biogas
- Bioethanol
- Bio jet fuel [8]

Non-energy products from algae;

- Carbohydrates
- Pigments
- Protein
- Therapeutics
- Nutraceutşcals (astaxanthin, omega three fatty acids, sterols etc.) [18]
- Food additives
- Feed
- Bio fertilizers
- Oxidants
- Pigments
- Cosmetics (Skin care, sun protection and hair care; tooth paste, lotions, creams, etc.)
- Nutritional compounds
- Vitamin supplements
- Pharmaceuticals (drugs, antioxidants, antimicrobials, anti-inflammatory agents etc.
- Biomaterials and bioproducts
- Textiles (alginate fibre for fabrics, algae derived oleic oil for textile lubrication)
- Chemicals (dyes and colorants, inks, defoamers, algae based resins, phycobiliproteins etc.)

Environmental applications;

- Bio-mitigation of CO_2 emissions using microalgae
- Bio-remediation of waste water and polluted soil using microalgae
- Heavy metal biosorption
- Soil additives, conditioners and fertilizers

Novel applications in other ındustries;

- Construction: Algae-sand composites as substitutes for brick, concrete, asphalt, and other civil engineering applications
- Electronics: Algae based batteries [19]

4. MICROALGAE APPLICATIONS WITH BIOREFINERY APPRAOCH

Algal Biorefinery includes cultivation of microalgae under suitable conditions, extraction of bioreactive products from harvested algal biomass, thermal processing (pyrolysis, liquefaction or gasification), extraction of high value chemicals from the resulting liquid, vapor and/or solid phases and reforming/upgrading of biofuels for different applications.

Production in microalgal biorefineries also consists of 2 stages as shown as Figure 2. In the first stage, the most suitable microalgae and the most suitable cultivation conditions for the target product are selected. The microalgae cultivation environment can be fresh water, saline water, or wastewater. The selected microalgae is introduced to the selected medium in a raceway pond, photobioreactor or a fermenter. Organic carbon and nutrients can also be added for efficient growth. When cultivation in wastewater is preferred, it is necessary to examine the wastewater characteristics well. It should be checked whether there are sufficient amounts of essential nutrients and trace elements in the wastewater we will use. In addition, parameters such as turbidity, color, or high amount of suspended solid etc. that may adversely affect microalgae cultivation should be checked and necessary pre-treatment processes should be carried out. Microalgae can be grown with a natural light source or with artificial lighting in the light-dark period, we have determined. In Stage 2, microalgae , which cultivated in first stage, are harvested by methods such as flotation, flocculation, centrifugation or ultrasound. Drying can also be done if necessary. The harvested microalgae are broken down by extraction methods such as solvent extraction, superficial fluid extraction, ultrasonic assisted extraction, enzymatic extraction and the target product can be obtained in the separation stage. The separated parts can be used directly or high value chemicals can be obtained by applying transformation processes such as fermentation, anaerobic digestion, transesterification, pyrolysis, gasification, combustion, hydrothermal liquefaction. At the end of all these stages, it is possible to obtain biofuels, lipid-based food products, pigments-based food products, protein-based food product, protein-based animal feed and other valuable chemicals.

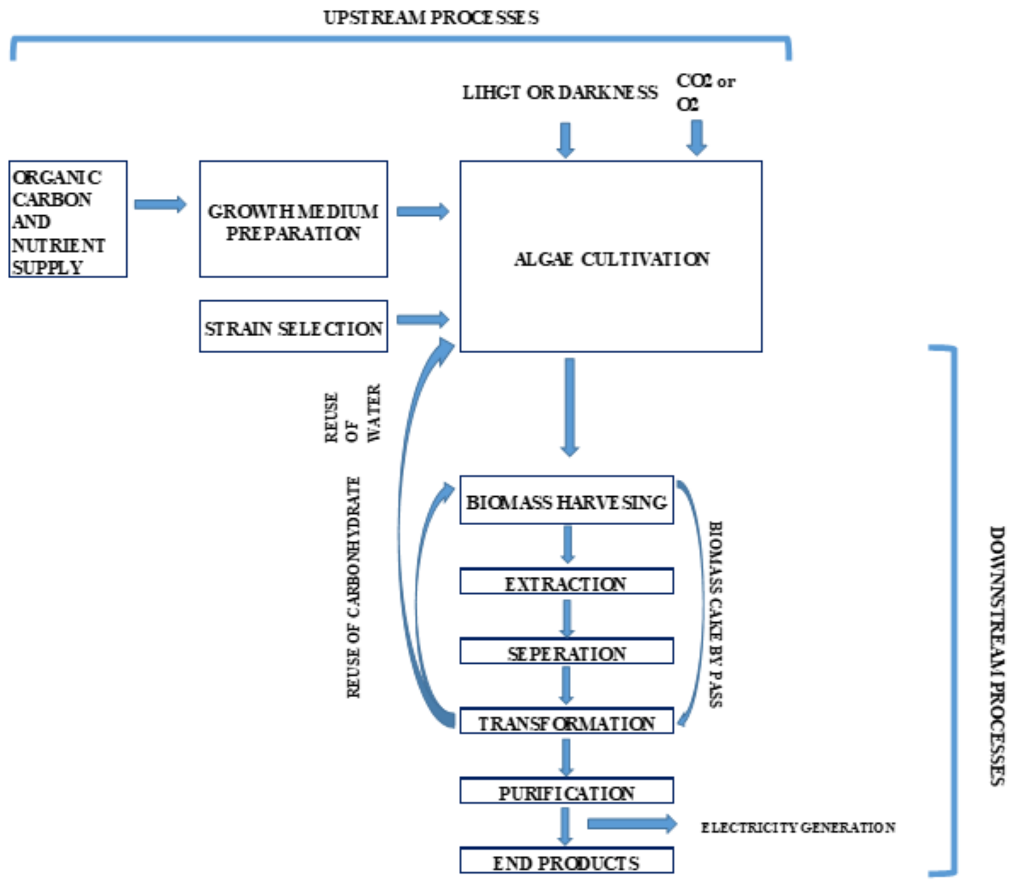

Figure 2. Generic algal biorefinery diagram

In order to understand how algal bioretention can work, its scope and potential, I designed an example of an algal biorefinery plant. I assumed that an algal biorefinery is built integrated into a textile factory. In this plant, the wastewater from the factory is fed to the biorefinery plant through the necessary pre-treatment processes. Microalgae is then fed to the wastewater. Microalgae are cultivated by providing appropriate temperature, pH, salinity, light-dark period. Microalgae consume N, P and C in the wastewater during growth and reproduction processes. Therefore, the wastewater is treated and made to meet the discharge standards. The produced microalgae are dried and pigment extraction can be made from microalgae by selecting appropriate methods. After pigment extraction, biodiesel can be obtained by extracting the lipids in the residual biomass. All remaining biomass can then be burned for energy cogeneration. The energy obtained can be used in the facility, enabling the facility to produce its own energy. The pigment obtained at the end of these processes can be used in dyeing processes in the textile factory. The treated water can be used with a secondary treatment or directly according to its intended use in the factory.

As we can see from the case study, algae biorefineries have great potential for the application of the circular economy in many sectors. With an integrated biorefinery, while multiple products can be obtained, at the same time wastewater can be treated and reused, part of the energy can be produced and one of the raw materials for the industry can be produced and wastes can be minimized.

4.1. Comparison of Algal Biorefinery and Plant-based Biorefinery

Currently most biorefineries are plant-based. There are only 3 biorefineries in Turkey. These plants produce bioethanol using sugar beet, wheat, corn and sugar molasses [20]. Unfortunately, there is not yet a large-scale biorefinery using microalgae as biomass. However, algal biomass appears to have significant advantages in operation. With their high photosynthetic efficiency, microalgae can be rapidly and efficiently utilized and converted into a large number of end products. Among the many advantages and environmental benefits listed in *Table 1*, the most important is that algal biomass does not require the use of agricultural land and freshwater resources. Thus, it is possible to protect our depleting resources and create added value while carrying out industrial activities in algal biorefineries.

Table 1. Comparison of algal biomass and plant-based biomass

Algal Biomass	Plant-based Biomass
Higher photosynthetic efficiency (3-8 %)[12]	Lower photosynthetic efficiency (0.5%)[12]
Higher growth rate	Lower growth rate
Higher biomass yields per hectare	Lower biomass yields
Higher CO_2 sequestration ability	Lower CO_2 sequestration ability
Can grow in soil, freshwater, saline and brackish water	Can grow only in soil with freshwater
No competition with farmland [8]	Needs suitable farmland (most are farm product)
Can be harvested almost all the year round with no seasonal breaks	Most can harvest once in a year
Less use of fertilizers and pesticides leading to less pollution	Needs fertilizers and pesticides for better growth
Microalgae have no stems or roots and lack highly resistant cell wall components, which are difficult to degrade.	Plants have lignocellulose and lignin as a cell wall components that are challenging to chemically break down and use.
According to do former statement, algae products and residual biomass are easier to use and combine.	According to do former statement, plant products are more difficult to use and combine
Growth time is approximately 2 weeks	Growth time is approximately 2-3 months
Contains much higher lipid content per biomass [8]	Contains less lipid content per biomass.
Cultivation can be done in the facility	Need to move from farmland to the facility[21]

5. CONCLUSIONS

Microalgae applications with the biorefinery approach are very promising. There are many studies on this subject in the literature. It would not be wrong to expect an increase in studies on multi-product biorefineries and energy production. In many countries, decisions have been taken to support biorefineries. At the 2022 Climate Council, Turkey took the following decision for the development of biorefineries. "Renewable energy-supported integrated biorefineries and innovative technologies should be developed for zero waste, circular economy and multi-product, renewable energy-supported integrated biorefineries and innovative technologies for the conversion of organic wastes and micro algae with high added value potential into products such as biofuels (solid, liquid, gas) and hydrogen through biochemical, thermochemical and hydrothermal technologies." [22]. Unlike Turkey, in Europe the relevant legislation was introduced much earlier. In Europe, in addition to the "Renewable Energy Act" of 2000, there are currently in place laws on the use of biomass in place of non-renewable resources when producing biofuels for transportation [10].

The potential of microalgal biorefineries is constrained by high capital cost and operating cost; lack of successfully implemented industrial-scale biorefinery processes; and lack of validated market applications for microalgal components [23]. It has become clear that microalgal biorefinery should be conducted in a multi-product approach and in a way that ensures global economics. More research is needed on multi-product biorefinery at industrial scale.

Algae systems that only aim to produce fuel do not seem feasible. The price of microalgal biodiesel is $21.11 ($/gal) (2013 US) compared to $3.91 ($/gal) (2013 US) for fossil biodiesel [24]. Selling at a lower price prevents the business from operating in a viable way. Making energy products more affordable may be possible through a multi-product biorefinery approach. If omega-3 oil extraction is integrated into this biodiesel production plant, the balance of income and expenses of the plant will completely change. If we extract omega-3 oil from microalgae, we will be able to earn 150 USD/kg for the omega-3 oil produced (US in 2019) [19]. Once high revenue generating products such as omega-3 oil, astaxanthin, lutein are produced, the plant can be made feasible with by-products and energy production and will pay for itself in a short time.

High-value microalgal products are typically much more expensive than conventionally chemically produced ones and can often be sold in specialized biomarkets. However, consumers tend to prefer natural products, especially in the cosmetic and food sectors. It may therefore be wise for algal production to target these sectors.

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BIOGRAPHY

Ebru Işık *works as a research assistant at Yıldız Technical University Environmental Engineering Department.*

Işık received her BSc in Environmental Engineering in 2020 from Bursa Technical University, Bursa, She is still Msc student at Yıldız Technical University Environmental Engineering Department.

She may be contacted at ebru.isik@yildiz.edu.tr