Valorisation of Algae Biomass into Biobased Products Using Emerging Technologies: A Review

Nikita Singh[1*], Manimagalay Chetty[2], Sudesh Rathilal[2] and Emmanuel Kweinor Tetteh[2]

Abstract— Recent energy demand and environmental concerns associated with fossil fuels makes algae biomass a desirable energy source. Algal biomass has a high organic content and a variety of metabolic properties that make it a promising resource for managing wastewater and sequestering CO_2, in addition to producing profitable biobased products. However, the operation and valorization of algae biomass on a large scale are accompanied by significant costs and setbacks. Therefore, the transition towards a biobased economy requires this study to examine emerging technologies that could utilize algae biomass as an industrialized feedstock from the wastewater settings. A comprehensive analysis of various green technologies of producing high-value products (lipids and hydrocarbons) from algae biomass was reviewed. The fundamental principles that limit the cultivation, extraction, and conversion of different types of algae biomasses for commercialization are discussed. Furthermore, the challenges, future research directions and potential opportunities of valorizing algae biomass were highlighted. It was noted that, exploring algae biomass towards sustainable waste management with resources recovery is viable for industrialization.

Keywords— Algae, biofuel, sustainability, wastewater

I. Introduction

Recent energy demands associated with the growing population demands, industrial expansion, urbanisation and environmental pollution have led to a shortage of fossil fuels. With 80 % of the global population depending on fossil fuel derived fuels, fossil fuel reserves formed from carbonaceous period approximately 286 – 360 million years ago are being depleted [1]. With the global demands expected to increase by 20 – 30 % by 2050, fossil fuels will be depleted by the next 50 years [2], [3]. Instead of the conventional exhaustible fuels, alternative energy sources and fuels are required; hence biofuels. However, there are significant challenges associated with biofuel production exist, mainly the 75 % production cost associated with biofuel production [1].

Microalgal biomass serves as an alternative renewable reservoir for biofuel production. Microalgae cultivation captures carbon dioxide during photosynthesis, reducing carbon dioxide emissions. Microalgae are unique photosynthetic organisms; which possess the ability to generate substantial biomass on terrestrial surfaces, unattainable by conventional agricultural crops. They are considered a third-generation feedstock, effectively avoiding competition with edible crops and sparing us from the adverse effects on food security, water resources, and deforestation [4]. Initially, microalgae had been used for medical purposes, particularly in the production of protein and antibiotics during World War II. During the 1970’s energy crisis, microalgae production gained interest, leading to research on hydrogen and methane production [5]. Currently, research focuses on wastewater treatment and carbon sequestration using various microalgae species. Integrating upstream and downstream processes can make lipid extraction and value-added products more economically viable.

Microalgal biofuels emerge as a feasible alternative for traditional fossil fuels, offering a solution to our energy crisis. Nonetheless, the utilization of microalgae in industrial settings encounters significant obstacles related to both energy consumption and expenses. The bio-refinery strategy, aimed at extracting essential constituents contained within microalgae, holds promise in this context. The process of cultivating, harvesting, breaking down cells, and extracting biofuels and valuable compounds constitutes crucial stages in the enhancement of microalgae for various purposes. Microalgae are composed of carbohydrates, proteins, and lipids ranging from 8 % to 69.7 %, 5 % to 74 % and 7% to 65 % respectively, making them valuable in various industries [3].
Microalgae-based fuel presents numerous benefits, such as its ability to naturally break down, environmentally sustainable nature, and its higher energy density. Biofuel derived from microalgae can be mixed with traditional fuels, creating a more versatile transportation fuel. Microalgae as a feedstock generate larger volumes of oil than any other feedstock [4]. Microalgae can thrive in both open and closed environments. They rely on specific nutrients and CO_2, which can be sourced from wastewater streams and fossil fuel combustion. When it

Nikita Singh[1], Green Engineering Research Group; Department of Chemical Engineering, Faculty of Engineering and The Built Environment, Durban University of Technology, Durban, 4001, South Africa

Prof Manimagalay Chetty[2], Cape Peninsula University of Technology, Bellville, Cape Town, 7530

Prof Sudesh Rathilal[2] , Green Engineering Research Group; Department of Chemical Engineering, Faculty of Engineering and The Built Environment, Durban University of Technology, Durban, 4001, South Africa,

Dr. Emmanuel Kweinor Tetteh[2] 2Green Engineering Research Group; Department of Chemical Engineering, Faculty of Engineering and The Built Environment, Durban University of Technology, Durban, 4001, South Africa

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comes to the oil content in microalgae, it can reach as high as 80 %, although levels typically fall within the range of 20 % to 50 %. For instance, Chlorella contains approximately 50 % lipids, while Botryococcus braunii stands out with an exceptional oil concentration of over 80 % [8]. Additionally, microalgae biofuel generation, a variety of bioactive chemicals with a wide range of applications in nutraceuticals, chemical and food industries, and pharmaceuticals can be generated (Fig.1) [7], [9]. Therefore, this review paper aims to emphasize the microalgae biorefinery concept in order to demonstrate its capabilities of being transformed into energy and high value products, microalgae potential and significance to energy, environmental and biobased demands, while the emerging technologies within the algae valorization route is highlighted. The limitations hindering cultivation, extraction and harvesting is highlighted together with the suggested solutions and directions of future research.

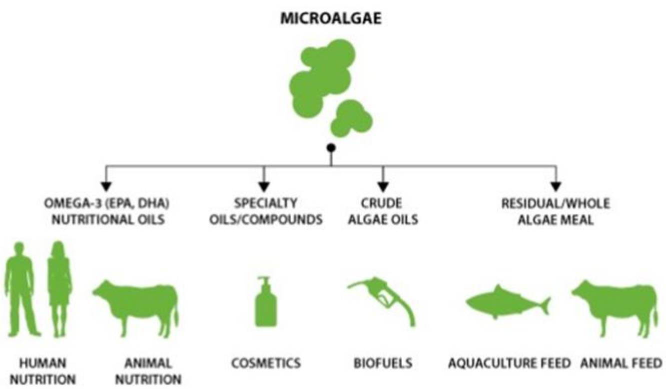

Fig. 1: Schematic of the various processing routes of microalgae

II. Sustainable algal biomass valorisation for biorefinery

Biorefineries employ a variety of techniques and equipment to create biofuels, electricity, and valuable chemicals from biomass, drawing inspiration from petroleum refineries that produce a range of products from crude oil. This approach is the transformation of biomass into marketable goods and energy. The process of establishing microalgae-based biorefineries encompasses stages like cultivating and harvesting microalgae, breaking down biomass, and extract and reclaim the necessary elements from the same batch of biomass, ultimately generating intact commercial products (Fig. 2). Biorefineries make us of various process methods and equipment to convert biomass into biofuels, power, and high-value chemicals. The goal of this algal biorefinery approach is to turn biomass into energy and commercial products [10]. Microalgae culture and harvesting, biomass cell disruption, and chemical extraction are all vital steps present in microalgae-based biorefining.

A. Cultivation of microalgae species

With the provision of necessary conditions such as CO_2 and sunlight, microalgal development can occur in wastewater ponds, photobioreactors, and agricultural land. Over 7 000 microalgae species have been discovered so far, with many more unknown [11], [12]. In order to create eco-friendly biofuels and other valuable products, it is crucial to minimize expenses associated with sourcing and production. Consequently, the selection of the appropriate microalgae strain plays a pivotal role in optimizing revenue through the production of biofuels and high-value byproducts. The composition of carbohydrates, lipids, and proteins within different microalgae species is of utmost significance in this context, hence the specific selection of strains for desired products. Lipids and hydrocarbon content is crucial for creating high-quality biofuel.

B. Challenges

The successful transformation of algal biomass into biofuels and valuable biomaterials relies on assessing its practicality and economic viability. It is imperative to employ efficient extraction techniques to obtain top-quality products and biofuels, reducing impurities, while tailoring the methods to the unique requirements of various bioproducts.

Open ponds for microalgae cultivation are particularly vulnerable to environmental factors because they do not have the means to regulate water temperature, light exposure, and evaporation. These variables can significantly impact the rate of microalgae growth. Additionally, external conditions like rainwater runoff, which can alter the salinity and pH levels, bank erosion leading to increased water cloudiness and leakage, and contamination from protozoa and bacteria due to the extensive cultivation area, all play a substantial role in determining microalgae productivity. In summary, open ponds lack control over crucial environmental parameters and are greatly affected by various external factors that can either enhance or hinder microalgae growth. Furthermore, because the environment contains only 0.03-0.06 % CO_2, mass transfer constraints are expected to slow microalgae cell growth. These systems achieve optimal performance in areas where there is ample sunshine and convenient availability of water.

In summary, these systems work most efficiently in sunny regions with abundant water access. In contrast to open ponds, closed photobioreactors are predominantly employed for the production of microalgae. Photobioreactors have been successfully used to produce significant amounts of microalgal biomass in a controlled environment. A photobioreactor (PBR) is a device that uses light-dependent organisms like algae for various biological reactions. PBRs are flexible systems that can be tailored to the specific needs of the algae being cultivated, enabling the growth of challenging species that wouldn't thrive in open ponds.

III. Valorisation of microalgae for the production of biofuels

Producing biofuels from microalgae is an eco-friendly energy source that utilizes natural materials as its source. The simplest way to transform microalgae into biofuel is through thermochemical conversion, which breaks down the organic components in microalgae biomass [13]. Alternatively, biochemical conversion methods employ various treatments, including physical, chemical, and biological processes, to convert biomass into useful products. Additionally, power plant emissions can be harnessed to supply CO_2 for microalgae cultivation; reducing the environmental harm

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associated with burning fossil fuels. Therefore, thermochemical conversion is the most direct approach, while biochemical conversion methods encompass various treatments.

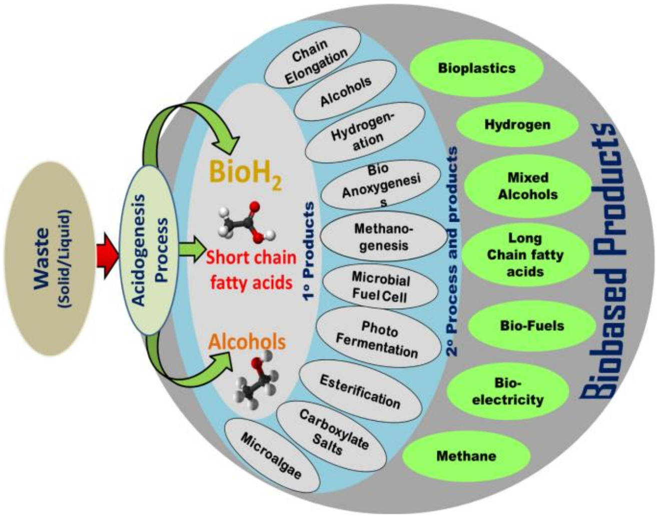

Fig 2. Schematic model of waste valorisation for bioenergy and bioproducts (Mohan *et al*., 2016)

A. Microalgae as a biodiesel source

Biodiesel stands out as a noteworthy biofuel, primarily because of its positive ecological attributes and its capacity to serve as an alternative to non-renewable fuels in various industrial and transportation applications. This renewable fuel is characterized by its non-toxic nature, biodegradability, and the ability to be recycled. Importantly, it can be readily used in both diesel and standard engines without any need for modifications [14]. The production of biodiesel is achieved through the transesterification process, which entails the separation and purification of microalgae biomass, which limits commercialization due to high energy requirements and water-adverse effects [15].

B. Microalgae as a source of bioethanol

Bioethanol, a significant form of biofuel, is derived from three primary sources: sugar and starch-based bioethanol, lignocellulosic bioethanol, and microalgal bioethanol [16]. Sugarcane is a frequently employed feedstock for production, whereas lignocellulosic and starch-based sources are more cost-effective options but necessitate hydrolysis as a step in the process. Microalgae varieties with elevated carbon content, such as Chlorella, Dunaliella, Chlamydomonas, and Scenedesmus, represent optimal candidates for bioethanol manufacturing. Brown algae are used as feedstock in modern agriculture due to their high carbohydrate content. Bioethanol is produced through drying, cell disruption, saccharification, and fermentation.

C. Microalgae as a source of biohydrogen

Hydrogen is an environmentally friendly and affordable energy source with the potential to support sustainable bioenergy in the future [17]. Biohydrogen, which is produced by microalgae through photobiological reactions using water and sunlight, is at the heart of the development. However, current methods are ineffective due to oxygen inhibiting the hydrogenase enzyme. Researchers have explored various techniques for producing biohydrogen, including supercritical water gasification, water electrolysis, methane reforming, coal gasification, oil and natural gas oxidations, thermal processes, and photo-fermentation [18], [19].

D. Microalgae as a source of biomethane

Biomethane or biogas is a renewable fuel derived from a variety of sources, including biomass and organic waste, using a process called anaerobic digestion [20]. One potential feedstock for producing methane is microalgae biomass, both in its natural form and after undergoing specific treatments. However, it is essential to pretreat microalgae biomass using various methods such as biological, mechanical, chemical, and thermal processes. To enhance methane production, enzymes, either of fungal or bacterial origin, can be employed, though they come with a cost. Another approach involves using crude enzymes to pretreat microalgae biomass, but this requires an extra step of enzyme production and extraction. An alternative solution is to cultivate algal biomass in the presence of organisms capable of producing enzymes, which could help address this challenge.

E. Microalgae as a source of bio-oil

Algae-derived energy has the potential to generate a dense, dark, and viscous fuel known as crude bio-oil. The production of this bio-oil can be accomplished by employing two distinct processes: pyrolysis and hydrothermal liquefaction. Interestingly, the bio-oil obtained from microalgae can exhibit a yield that is 5-25 % higher than their inherent lipid content [21]. Pyrolysis, a technique involving the high-temperature heating of organic compounds, encompasses three subcategories. Consequently, bio-oils may contain a variety of components such as aldehydes, cresols, acids, linear hydrocarbons, and nitrogenous compounds [22]. On the other hand, hydrothermal liquefaction entails using hot compressed water to convert moist microalgal biomass into a liquid fuel.

F. Fine chemicals and bioactive compounds production from microalgae

Microalgae are a valuable industrial resource for non-fuel materials like lipids, proteins, carbohydrates, and vitamins. It can also be used for food, cosmetics, pesticides, organic fertilizer, and electricity generation [23].

G. Microalgae in agriculture

Microalgae offer environmentally friendly options for agriculture, functioning as eco-fertilizers, soil enhancers, and supplements for animal feeds. When used in rice farming alongside marine or aquatic microalgae, crop yields saw a notable boost, increasing by 7 – 20.9 % [24]. Additionally, microalgae contribute to soil enrichment by capturing carbon dioxide and nitrogen, thereby reducing the expenses associated with essential macro and micronutrients required for achieving high crop yields. Furthermore, these microorganisms generate plant growth regulators and enhance plant defense mechanisms, providing a sustainable alternative to detrimental chemical fungicides [24], [25].

H. Microalgae as source of animal feed

Microalgae are valuable food sources for aquaculture and animal feed due to their high-quality compounds, vitamins, antioxidants, and minerals [26] – [28]. They are suitable for ingestion and contain biochemical ingredients. Proteins make up 50-70% of microalgae structure [29]. Common microalgae organisms in aquaculture include Spirulina, Isochrysis, Chaetoceros, Chlorella, Nannochloropsis, Tetraselmis, Thalassiosira, and Skeletonema. Spirulina is a common dietary supplement for tropical fish, valued for its abundant pigments that enhance their growth and desirability as food [30]. Microalgae biomass, particularly rich in polyunsaturated fatty acids (PUFAs), can enhance the quality of meat in pigs, broilers (chickens), and lambs. When poultry are fed with microalgae that are rich in PUFAs, these beneficial fatty acids can accumulate in their eggs, thereby improving the nutritional value of broiler chickens. Moreover, wastewater that contains significant nutrient levels can serve as a valuable resource for both aquaculture and livestock feed, reducing the emission of greenhouse gases and the need for costly wastewater treatment.

I. Microalgae as a source of medicine

Microalgae offer a wide range of therapeutic benefits for human health, including anticancer, antiviral, antibacterial, cardiovascular, and anti-inflammatory effects [31]. They contain bioactive compounds like carotenoids and fatty acids that are beneficial for conditions such as macular degeneration, neurodegenerative diseases, and heart health. Astaxanthin, a powerful antioxidant found in microalgae, has various health-promoting properties and can be used in nutraceuticals and food products. These compounds also protect against UV damage and nerve-related issues.

J. Microalgae as a pigmet

Microalgae, rich in naturally colored pigments, can be used sustainably to produce food colourants. These pigments, including carotenoids, chlorophylls, and phycobiliproteins, are precursors to vitamins, coloring agents, biomaterials, cosmetics, and pharmaceuticals [32]. Carotenoids are crucial for oxygenic photosynthesis and are used in livestock feed, food products, and cosmetics. Phycobiliproteins, found in red algae and cyanobacteria, are used in various health sectors for anti-inflammatory, anti-allergenic, antioxidant, antiviral, anticancer, and neuroprotective substances [33].

K. Microalgae as a source of human food

Various microalgae species such as Spirulina, Chlorella, and Dunaliella are frequently incorporated into food products to improve their nutritional content and promote better health [34]. Chlorella, in particular, is a widely accepted global food replacement. Brown algae contain alginates, which offer various health advantages. Additionally, microalgae like Thalassiosira, Isochrysis, Tetraselmis, Chaetoceros, and Nannochloropsis contain valuable health-enhancing compounds such as DHA and EPA, known for their heart-protective effects [35]. However, the green color of these microalgae can influence consumers' perceptions of taste and texture, which limits their utilization in everyday consumer goods.

L. Microalgae as a source of cosmetics

Microalgae-derived components could be beneficial for the cosmetics industry in producing personal care products. These products improve skin structure and appearance, with active ingredients formulated for specific skin types. Algae extracts are used in anti-aging agents, moisturizing agents, wound healing agents, and hair growth promoters [34] – [36]. They also have potential as antimicrobials, expanding the cosmetics field. Eyeshadow can be produced from pigments from microalgae, and extracts from Chlorella vulgaris enhance collagen repair pathways.

IV. Future Directions

Microalgae harbors great potential in mitigating carbon dioxide emissions, wastewater treatment, and the production of biofuels, offering a pathway to a sustainable future. Nevertheless, it grapples with issues related to energy input and efficiency, necessitating more streamlined methods. Future implementation should emphasize long-term sustainability and environmental advantages, especially in developing nations. Additionally, comprehensive analyses are required to identify suitable microalgae strains for biofuel production, along with considerations for the optimal biomass quantity needed for successful extraction.

Over the last 25 years, the International Energy Agency (IEA) has noted a consistent 1.8 % annual increase in global energy consumption, leading to a worldwide energy crisis. To meet this surging demand, alternative technologies have been adopted, encompassing 1st, 2nd, and 3rd generation biofuel production [38]-[42]. 1st generation biofuels, such as biodiesel, bioethanol, and biogas, are linked to edible oils and other commodities, provoking the contentious food-versus-fuel debate. On the other hand, 2nd generation biofuels, derived from lignocellulosic biomass (LCB) and waste materials, offer a sustainable alternative with a carbon-neutral or even carbon-negative status due to reduced CO_2 emissions [43]. Yet, the commercial viability of 2nd generation biofuel production is hampered by technical hurdles, notably lignin removal. An analysis projected production costs of 1st and 2nd generation biofuels relative to fossil fuels until 2020 [45]. Their findings suggest that waste oil-derived biodiesel is the most cost-effective biofuel at a crude oil market price of €100/barrel. In 2020, ethanol from LCB and biodiesel from waste oil and palm oil are expected to be more economical than fossil fuels. Nevertheless, the study raises concerns regarding the availability of adequate feedstock for the transition [14],[46].

The emergence of 3rd-generation biofuel technology, employing microalgae as a feedstock, has garnered attention due to its potential to address global environmental issues like global warming and oil spills. Algal biomass offers advantages such as shorter generation times, lipid accumulation, minimal freshwater requirements, and no competition with human food supplies. Nonetheless, few cost-effective technologies have materialized, particularly in developing countries. The integrated approach or biorefinery model leverages the entire algal biomass for biofuel and bioproduct production, with residual biomass employed for biohydrogen and biogas generation. To make 3rd generation biofuels competitive with conventional fuels, costs must be reduced substantially, aiming to reach ten times lower than current costs. To meet the projected bioenergy demand by 2022, approximately 36 billion gallons of biofuel from algal biomass will be required, necessitating considerations of power consumption, water usage, carbon, energy, and nutrient sourcing [48]. The production of algal biomass and subsequent processes entail additional costs, making sustainability a formidable challenge. The primary objective for many biofuel industries is to implement innovative new technologies with minimal waste generation and maximal outcomes.

The amalgamation of wastewater treatment with microalgae cultivation for biomass production has gained traction within 150 commercial sectors worldwide [49]. Notably, major global companies have embarked on large-scale microalgal biofuel projects and have initiated a dual pilot scheme for biofuel production from an algal-based biorefinery.

In Japan, over thirty companies and organizations formed the "Initiatives for Next Generation Aviation Fuels" group in 2014, with the aim of utilizing domestically sourced aviation biofuels by 2020. Japanese microalgal company Euglena, in partnership with Chevron Lummus Global, announced plans in 2015 to establish the nation's first demonstration plant for jet fuel production from microalgae. This facility is projected to yield approximately 33,000 gallons of jet biofuel annually for All Nippon Airways (ANA), with aspirations for full commercialization in the 2020s.

According to the National Algal Biofuels Technology Roadmap issued by the U.S. Department of, the successful commercialization of microalgal fuel hinges on advancements in high-value co-products like pigments and renewable polymers. Progress in metabolic engineering, synthetic biology, and genomics, coupled with innovations in closed photobioreactor (PBR) systems and raceway ponds, as well as the development of novel lighting, harvesting, and extraction systems, is propelling the commercialization of microalgae biofuels.

Furthermore, synthetic biology techniques for genetically modifying microalgae to enhance wastewater treatment have the potential to substantially boost growth and biomass accumulation. The use of next-generation sequencing knowledge has deepened the scientific understanding of microalgal genomes, particularly the genes involved in metabolic responses. Metabolic engineering plays a pivotal role in advancing synthetic biology, which aims to optimize pathways in industrial biotechnology for improved production of valuable chemicals, biopharmaceuticals, bioenergy, and waste degradation.

Recent studies have outlined five strategic imperatives to expedite the commercialization of microalgae biofuels: faster production, cost-effectiveness, enhanced quality, marketing strategies for co-product fractions, and a concerted effort to minimize waste [40]-[49]. Microalgae species with up to 50 % oil content offer additional resources in the form of carbohydrates and proteins, which can be utilized for biodiesel and ethanol production. These proteins also have applications as feed additives for poultry, livestock, and fish. Microalgae present itself as a sustainable, carbon-neutral source of transportation biofuel, and these strategies have the potential to reduce production costs and accelerate commercialization efforts [50]-[54].

V. CONCLUSION

The predominant focus of microalgae production has primarily revolved around the generation of biofuels, thereby limiting its broader utility across various sectors, such as cosmetics, pharmaceuticals, and agriculture. In contrast, the processing of biogas effluents stands out as a promising avenue for optimizing bioprocesses and yielding a diverse array of bioproducts, including proteins, biofuels, and biofertilizers. The treatment of wastewater through the utilization of algal consortiums is an efficient and eco-conscious approach, and it relies significantly on genetic modification and strain selection to advance the underlying technology.

The potential of algal biomass is substantial, offering environmentally friendly, sustainable, and cost-effective resources for the production of biofuels and bioproducts. The development of biorefinery models and the integration of various processes, such as biodiesel, biohydrogen, and biofertilizers, serve to enhance the economic feasibility of microalgae production. In addition, environmentally friendly techniques like microwave-assisted lipid extraction, anaerobic digestion, and bioethanol fermentation play a pivotal role in advancing these endeavors.

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