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Conversion of algal biomass into renewable fuel: A mini review of chemical and biochemical processes

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Microalgae are a vital resource for the coming years to address the concern of decrease in oil reserves and the negative impacts of fossil fuels on the environment. Their utilization is crucial for a wide range of industrial applications. Depending on the strain, microalgae contain a variety of chemical components and can be treated biochemically or thermochemically. This review thus focuses on the biochemical mechanisms that are used to convert algal biomass into sustainable fuel, including the challenges and potential of those processes. Microalgae have been shown to be a viable third-generation alternative to conventional biofuel feedstocks. The optimum production of biofuel depends on the proper selection of microalgae species based on their lipid, carbohydrate, and protein content in order to produce high-guality, sustainable biofuel. Nannochloropsis gaditana can contribute to a maximum biodiesel yield of 96.47%, whereas Nannochloropsis oculata can produce the least (25%) through the biochemical process of transesterification. Higher yields of microalgae-derived gaseous, solid and liquid fuels can be achieved by pre-treating microalgal biomass and then employing bioconversion processes such as photofermentation and hydrothermal carbonization.

KEYWORDS

microalgae, biochemical process, sustainable fuel, greenhouse gas emission, biomass

1 Introduction

The pressing demand for energy, the diminishing sources of fossil fuels, and the mounting environmental concerns all call for a promising alternative fuel including biofuel (biodiesel, biomethane, bioethanol etc.) (Mofijur et al., 2013a; Chuah et al., 2016; Chuah et al., 2017). Microalgae, as a feedstock for biofuels have demonstrated a significant amount of potential. This is as a result of the fact that it matures with copious mass creation in a matter of days as opposed to terrestrial crops and plants, which can take anything from a few months to many years to reach this stage of development (Wang et al., 2007; Yu et al., 2017; Chia et al., 2018). The primary benefits of using biofuels from the microalgae are that they do not require the use of potable water, they can be grown on land that is not suitable for agriculture, they require only simple nutrients like CO₂ and sunlight, they do not require the use of herbicides or pesticides during cultivation, they can use carbon-neutral feedstock, and they can produce high-quality

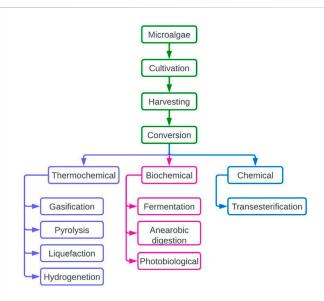


FIGURE 1

Various conversion technologies for biofuel production, modified from (Suali and Sarbatly, 2012).

pyrolytic materials (Singh et al., 2011; Lee and Ofori-Boateng, 2013; Debiagi et al., 2017; Chia et al., 2018; Gan et al., 2018). In addition, the high photosynthetic efficiency of microalgae, which ranges from 6% to 8%, when compared to the photosynthetic efficiency of terrestrial biomass, which ranges from 1.8% to 2.2%, as well as the high CO_2 fixation by microalgae, makes them excellent biofuel feedstocks and natural environment remediators (Kumar et al., 2017; Yu et al., 2017; Yu et al., 2018; Brigljević et al., 2019). In addition to this, it has been observed that the bulk of microalgae is composed of more than 70% fat when measured based on their dry weight (Liang et al., 2010). Because of their high lipid content, microalgae are an important component in the manufacture of biofuels. Cultivating microalgae can, over the course of time, result in both the production of economically viable feedstock and the decrease of greenhouse gases.

The cultivation of microalgae for commercial purposes takes place in a particular sort of bioreactor that creates ideal growth conditions, resulting in high levels of output. At this time, open raceway ponds and closed photobioreactors are both utilised for the production of microalgae, and the selection of one or the other is determined by the particular requirements. Raceway ponds that are open to the environment are frequently used for the treatment of wastewater, whereas closed photobioreactors are typically utilised for the production of pharmaceutical and value-added goods. The quantity of biofuel produced and the quality of that biofuel are both highly dependent on a number of parameters, including the properties of the microalgae, the conditions of the production process, the catalyst type and dosage, and the configuration of the reactor (Azizi et al., 2018). The effect of these elements should be thoroughly investigated and modified in order to get the best output and quality of biofuels from microalgae. This will allow to reach goals. Few researchers already studied different microalgae conversion processes (Rowbotham et al., 2012; Marcilla et al., 2013; Chen et al., 2015a; Elliott, 2016). A large number of macromolecular components serve as substrate for the biochemical conversion process, which is one of these processes. As a result, the benefit of using microalgae in the biochemical conversion

process is that it results in a reduced level of process complexity while simultaneously providing an energy form together with a mineralized digestate that is rich in beneficial nutrients. Thus, the purpose of this mini review is to highlight the utilisation of different biochemical processes and the challenges and future prospects of those processes to convert algal biomass into sustainable fuel.

2 Conversion technologies of microalgae into biofuels

Converting microalgae into biofuels can be accomplished through the use of a variety of different technologies. As shown in Figure 1, these conversion methods can be categorised into two primary categories: biochemical and thermochemical. Because certain biomass feedstocks include high levels of lipids, it is possible to extract those lipids using either physical or chemical separation methods. After that, the triglyceride portion of the extracted lipids can be converted into biodiesel by using the transesterification process. The biochemical conversion processes also result in the production of biogas or ethanol, and the conversion itself is a somewhat slow process, typically lasting hours, days, or weeks depending on the kind of feedstock (Bridgwater, 2010). Thermochemical conversion including pyrolysis and gasification process, on the other hand, results in the production of several products in a relatively short amount of time and the quality of the products that are intended for consumption may frequently be improved with the application of catalysts.

One of the most important steps in ensuring that the production of biofuel is both economically viable and environmentally sustainable is making the choice of the appropriate conversion technology. At this point in time, there are no obvious advantages that can be demonstrated between the thermochemical and biochemical routes. However, according to a review that was done by Sims and colleagues (Sims et al., 2010), thermochemical conversion is regarded as being more favourable. The properties of the feedstock are one of the most significant challenges for biochemical conversion. Feedstock modifications, such as those involving pre-treatment processes, call for a significant investment of capital, which, in turn, drives up production costs. In addition, the efficiency with which biomass may be converted into biofuel by using biochemical processes is quite low. In addition, the biochemical pathway could only result in the production of a single type of end product for each application, in contrast to the thermochemical pathway, which may result in the production of multiple types of end products from a single operation. In the next subsections, a concise discussion of each kind of conversion technology is presented.

2.1 Chemical and biochemical conversion technologies of microalgae

2.1.1 Transesterification of microalgae

The typical process that is utilised to convert the triglyceride found in microalgal lipid into biodiesel is called transesterification (Sinha et al., 2008; Rajan and Senthilkumar, 2009). This is the reaction that occurs when TG is combined with an acyl-acceptor (Fan and Burton, 2009; Helwani et al., 2009). Acyl-acceptors might come in the form of carboxylic acids, alcohols, or even another ester. When alcohol is used as the acyl-acceptor in transesterification, glycerol is produced; however, triacylglycerol is produced when ester is utilised (Ma and Hanna, 1999; Dubé et al., 2007; Ranganathan et al., 2008; Sharma et al., 2008; Robles-Medina et al., 2009). According to the principles of stoichiometry, 3 mol of alcohol are needed for every mole of TG. In most cases, however, a greater molar ratio of alcohol is employed in order to accomplish the highest possible level of biodiesel generation. This molar ratio changes depending on the type of feedstock that is used, the type of catalyst that is used, the temperature, and the amount of time that the reaction takes. Methanol, ethanol, and propanol are the three types of alcohol that are utilised most frequently (Mofijur et al., 2013b; Mofijur et al., 2014; Rozina et al., 2022). In point of fact, the yield of biodiesel is not affected by the type of alcohol that is used; rather, the selection of alcohol is determined by cost (Al-Zuhair et al., 2007; Sinha et al., 2008).

The process of transesterification that makes use of a catalyst is referred to as a catalytic transesterification process, whereas the process that does not make use of a catalyst is referred to as a non-catalytic transesterification process (Gerpen, 2005; Meher et al., 2006; Marchetti et al., 2007). In addition, a catalytic process might be one of two categories: homogeneous or heterogenous, and this classification is determined by the catalyst that is being employed (Fjerbaek et al., 2009; Lin et al., 2009). It has been reported that the heating value of biodiesel made from microalgae is 41 MJ/kg (Xu et al., 2006) and this value is in accordance with the ASTM D6751 standards (Li et al., 2007). According to a number of studies, the enzyme that comes from lipase is fantastic for the process of converting a variety of vegetable oils to methyl ester. The transesterification process in generally take place at 35–50°C at atmospheric pressure and a molar ratio of 3:1–6:1 (Fjerbaek et al., 2009; Mata et al., 2010).

2.1.2 Fermentation

The production of ethanol from organic substrates like sucrose, bagasse, cellulose, or starch is the goal of the metabolic process known as fermentation (McKendry, 2002a; Lee and Lee, 2016). The fermentation of starch, sugar, and cellulose found in microalgal biomass is the primary route that leads to the synthesis of ethanol from microalgae (Kim et al., 2011), with starch making up the majority of the carbohydrate content and having a potential range of up to 60 dw% depending on the culture conditions (Nahak et al., 2011; (Brányiková et al., 2011). Controlling the amount of nitrogen or iron present during culture of microalgae can result in increased starch production (Liu et al., 2008; Dragone et al., 2011). In its most basic form, fermentation can be broken down into two categories: (Chuah et al., 2016) aerobic and (Chuah et al., 2017) anaerobic, with the distinction between the two based on whether or not the process requires oxygen.

Before microalgae biomass or starch can be fermented, it must first undergo pretreatment in the form of milling, which turns the biomass or starch into sugars. Next, the sugars are combined with *Saccharomyces cerevisiae* yeast and water in a fermenter for the fermentation process (Demirbaş, 2001). After fermentation, the diluted alcohol that was generated is put into a holding tank where it waits to be distilled. The ethanol concentration in the diluted alcohol product typically ranges from 10% to 15% (McKendry, 2002a). The product can be purified through the distillation process, which also results in the production of concentrated ethanol that has a purity level of 95% and is therefore appropriate for use as a supplement or substitute for transport fuel (McKendry, 2002b). This fermentation process uses less energy because the CO_2 produced can be used to grow microalgae and the leftover material can be recycled as a medium for microalgae growth or used as animal feed (McKendry, 2002a; Milledge et al., 2014).

There are four primary processes that take place during the fermentation of ethanol. Ethanol has replaced gasoline in many vehicles over the last decade because to its ability to reduce emissions of CO₂ and many harmful pollutants (CO, NO) during combustion (Demirbas, 2008). As a transportation fuel, bioethanol is widely available on the market and is utilised often (Walker, 2010). Nevertheless, bioethanol has a few downsides, including the fact that it is caustic, has a low energy value, is hazardous to the ecology, and has a low vapour pressure. However, in order to achieve long-term benefits and sustainability, additional efforts are required to upgrade bioethanol to a higher quality fuel that can stand alone and is compatible with fossil fuel. At the moment, bioethanol is ready to be integrated with the fuel that is already being used for transportation. C. vulgaris is a type of microalgae that is excellent for the production of bioethanol. This species has a high starch content (about 37%), which enables it to achieve up to 65% of ethanol conversion (Adeniyi et al., 2018). In addition to Chlamydomonas, Dunaliella, Scenedesmus, and Spirulina, which all contain more than fifty percent starch, there are also species that are thought to be promising candidates for the synthesis of bioethanol (Hu et al., 2012). Table 1 provides a summary of the findings of studies conducted on the production of biofuel using various biochemical processes.

2.2 Anaerobic digestion of microalgae

When the biomass to be converted has a high-water content, the biochemical process of anaerobic digestion becomes crucial. In this process, biogas, NH₃, and CO₂ are produced, along with other undesirable gases like H₂S from the biomass's organic content (Mahmudul et al., 2021). Microalgae biomass, both pre-treated and untreated, and lipid extraction leftovers can be employed to generate methane (Siddiki et al., 2021). Steps of hydrolysis, fermentation, and methanogenesis follow one another in the digestive process. First, the organic matter is broken down into soluble sugars, and then the bacteria ferment those sugars to produce methane and carbon dioxide. As a result of the digesting process, a gas is produced that contains 20%-40% of the lower heating value of the feed in terms of energy. To get the best possible end result from the anaerobic digestion process, it is necessary to tune the hydraulic retention, organic loading parameters, pH, and temperature (Ahmed et al., 2021). The majority of current biogas research is devoted to improving wastewater treatment and finding ways to integrate biogas generation with other algal-based manufacturing techniques. In addition to lowering odours, hazardous gas emissions, and oxygen demand in wastewater, anaerobic digestion of microalgae has a few other advantages.

3 Challenges of chemical/biochemical conversion of microalgae

Capital-intensive efforts to convert algae into biofuels have been advocated for on the basis of the plant's rapid expansion, manageable size, and high oil content. There are a number of

Biochemical process	Microalgae species	Biodiesel yield	References
Transesterification	Aurantiochytrium sp.	89.50%	Kim et al. (2016)
	Botryococcusbraunii	95%	Hidalgo et al. (2015)
	Chlamydomonas sp.	101%	Chen et al. (2015b)
	Chlorella pyrenoidosa	10.50%-92.50%	Cao et al. (2013), Cheng et al. (2013)
	Chlorella vulgaris	51.54%-100%	Levine et al. (2010), Nguyen et al. (2020), Malekghasemi et al. (2021)
	Nannochloropsis gaditana	96.40%	Im et al. (2015)
	Nannochloropsis oculata	25%	Jafari et al. (2021)
	Nannochloropsis sp.	20.90%-85.80%	Koberg et al. (2011), Patil et al. (2011), Wahidin et al. (2016)
Biochemical process	Microalgae species	Bioethanol yield	References
Fermentation	Chlorella sp.	0.43 g ethanol/g sugars	Seon et al. (2020)
	C. Vulgaris	0.07 g ethanol/g microalgae	Yu et al. (2020)
	Chlorella sp.	0.19 g/g glucose	Abdulla et al. (2020)
	Chlorella Vulgaris	33.21 g/L	Bhuyar et al. (2021)
	Arthrospira platensis, chlorella marina, and ulva linza	45.49%	Ismail et al. (2020)
	Saccharomyces cerevisiae	0.46 g/g glucose	Shokrkar et al. (2017)
	Nannochloropsis oculata and tetraselmis suecica	7.26%	Reyimu and Özçimen (2017)
	Porphyridium cruentum	2.98 mg/mL	Kim et al. (2017)
	Saccharomyces cerevisiae	18.57 g/L	El-Mekkawi et al. (2019)
	Saccharomyces cerevisiae	0.46 g ethanol/g glucose	Shokrkar et al. (2018)
	Chlamydomonas sp.	0.22-g/g residual biomass	Kim et al. (2020)
	Chlorella	0.28 g ethanol/g microalgae	Phwan et al. (2019)
Biochemical process	Microalgae species	Biomethane yield	References
Anaerobic digestion	Porphyridium cruentum	179 mL CH ₄ /g VS	Kendir Çakmak and Ugurlu (2020)
	Chlorella vulgaris	168.9 mL CH ₄ /g COD	Llamas et al. (2021)
	Haematococcus pluvialis	91.9 mL CH ₄ /g VS	Hosseini et al. (2020)
	Chlorella pyrenoidosa	147 mL CH ₄ /g VS	Kumari et al. (2021)
	Chlorella sp.	194.63 mL CH ₄ /g VS	Wu et al. (2020)
	Chlorella sp.	0.14 m³/kg	Solé-Bundó et al. (2020)
	Chlorella vulgaris	0.062 m ³ CH ₄ /kg VS	Assemany et al. (2019)
	Scenedesmus obliquus	0.16 m ³ CH ₄ /kg VS	Assemany et al. (2019)
	Scenedesmus sp.	0.185 m ³ CH ₄ /kg VS	Zamorano-López et al. (2019)
	Nannochloropsis limnetica	0.41 m ³ CH ₄ /kg VS	Tsapekos et al. (2018)
	Chlorella sp.	0.2 m ³ CH ₄ /kg VS	Solé-Bundó et al. (2019)
	Nannochloropsis limnetica	0.41 m ³ CH ₄ /kg VS	Tsapekos et al. (2018)
	Chlorella sp.	0.26 m3 CH4/kg VS	Solé-Bundó et al. (2017)

TABLE 1 Summary of the findings of studies conducted on the production of biofuel from microalgae using various biochemical processes.

challenges that need to be addressed before algae can emerge as a financially feasible substrate to replace petroleum and, thus, decrease CO_2 release. These challenges range from where and how to cultivate these algae to advancements in oil extraction

and fuel processing (Hannon et al., 2010). Some of the challenges of converting microalgae into biofuel through chemical/biochemical conversion processes (Siddiki et al., 2022) are discussed as follows.

- The process of conversion is greatly governed by environmental factors.
- The products made through biochemical processes are more selective and can be processed at lower temperatures.
- Ideally suitable for processing algal biomass with a moisture content higher than 50%.
- The first step in this process of transformation is the pretreatment of the feedstock.
- The slower reaction rate necessitates longer residence times for product formation.
- Biological conversion is a major bottleneck that reduces productivity. More money would need to be spent on infrastructure upgrades, like a larger reactor, to accommodate the increased production.
- To achieve any kind of feasible findings, the use of bacteria, enzymes, or chemicals is essential. Sludge, an undesirable waste product, is produced and needs to be treated in some way.
- Due to the biological nature of the conversion process, the amount of production is relatively low.
- In most cases, limited to a few products and additional microorganisms are required to produce additional products.

4 Future prospects of chemical/ biochemical conversion of microalgae

There are challenges, but at the current rate of development, biofuels derived from microalgae may be capable of competing with existing energy sources within decades. Industrial-scale chemical/ biochemical conversion of microalgae into biofuels will require concerted efforts to optimise strains and increase production volumes. As a result, on the basis of the most recent state of the art, the following are some proposals for potential future developments.

- The productivity of a specific strain of microalgae can be increased to some degree by updating the design of the photobioreactor, regulating the physical conditions, giving growth nutrients, and adding metal ions. Further progress can be made by improving strains utilising recombinant DNA technology, which could lead to enhanced metabolic pathways that concentrate more biofuel-grade compounds.
- In order to make the process of algal harvesting more efficient, it is possible to make use of cutting-edge methods like fungimediated harvesting and the application of tailored nanoparticles. This will make it easier to separate the farmed microalgae from the broth in which they were grown.
- The amount of biofuel that can be extracted from harvested microalgae depends on the pre-treatment processes that are employed. Additionally, the linking of more than one pretreatment processes has emerged as a promising strategy; nevertheless, this technique requires additional study before it can be used at industrial scales.
- The application of physicochemical and physical pre-treatments in combination have shown the enhancement of carbohydrate release from algal biomass.
- The improvement of efficiency with which enzymes transform sugar into its constituent molecules.

• The enhancement of fermentation efficiency through nutritional supplementation of both liquid and gaseous media.

5 Environmental viability assessment of microalgal biofuels

Microalgae are able to withstand and absorb significantly higher quantities of CO₂ than terrestrial plants. Because of this, microalgae are able to utilise CO₂ released from petroleum-based power stations or other industrial sources, which can reduce the production of glasshouse gas (Nigam and Singh, 2011). It is possible to transform the entire algal biomass as well as extracts of algal oil into various forms of fuel. Because algae are able to extract nutrients like nitrogen and phosphorus from a wide range of wastewater sources, they are able to provide a sustained bioremediation of these wastewater sources, which has benefits for both the environment and the economy (Shilton et al., 2008). Carbon credits can be generated through the use of algal biofuels thanks to their ability to connect the generation of CO₂-free fuel with the sequestration of CO₂ from other power industries (Dismukes et al., 2008). When compared to terrestrial feedstock crops, algae have a number of advantages that make them more desirable. Despite the fact that their development requirements are comparable to those of terrestrial plants, they make very effective use of the resources available to them and as a result, they have great productivity despite using a relatively small amount of water (Brown and Zeiler, 1993; Chelf et al., 1993). The algae take in the additional CO₂ that is present, storing it as biomass as a result of their accelerated rate of development. Microalgae offer other benefits in addition to their potential for capturing CO₂ from fossil fuel power plants. This is because direct CO₂ capture procedures are preferred to indirect CO₂ capture processes. Passing flue gases directly through a media where microalgae can grow is an efficient technique to capture the CO₂ in such streams (Benemann, 1997). While it's likely to be extremely expensive to apply CO₂ directly to terrestrial crops via enclosures, an indirect technique that uses flue gases to stimulate land species could be cost-effective while being much less direct and less efficient (Packer, 2009).

6 Conclusion

Increased interest in microalgae biofuel production has been driven by rising concerns about the use of fossil fuels, greenhouse emissions, and the conflict between food and fuel when it comes to conventional biofuel sources. This study reviewed the biochemical mechanisms used to convert algal biomass into sustainable fuel, as well as its challenges and potential. Microalgae were found to be the largest renewable, clean energy resource with the potential to replace fossil fuels. Cultured microalgae in a photobioreactor could meet the biomass requirements for continuous biofuel generation in addition to repairing CO₂ emissions and treating wastewater. The best method for converting wet biomass into biofuel is the biochemical conversion process provided that the biomass's moisture content is higher than 50%. Although microalgae hold great potential, neither upstream nor downstream methods now available can completely tap into this potential. Consecutive growth of microalgae requires extremely efficient and cost-effective processing in order to provide sustainable and high-quality biofuel production and reduce reliance

on fossil fuels. However, there is still a significant knowledge gap in microalgal biofuel research since it is difficult to compare the chemical composition of different feedstocks to that of synthesized products. To bridge the gaps for future development, more comprehensive characterisation studies are needed.

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