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Algae biogas production focusing on operating conditions and conversion mechanisms – A review

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A R T I C L E I N F O

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A B S T R A C T

Global warming is the result of traditional fuel use and manufacturing, which release significant volumes of CO_2 and other greenhouse gases from factories. Moreover, rising energy consumption, anticipated limitations of fossil fuels in the near future, and increased interest in renewable energies among scientists, currently increase research in biofuels. In contrast to biomass from urban waste materials or the land, algae have the potential to be a commercially successful aquatic energy crop, offering a greater energy potential. Here we discuss the importance of Anaerobic Digestion (AD) for enhanced biogas yield, characterization, and comparisons between algae pretreatment methods namely, mechanical, thermal, microwave irradiation, and enzymatic and catalytic methods. The importance of anaerobic digestion enhances biogas yield, characterization, and comparisons between mechanical, thermal, microwave irradiation, and enzymatic and catalytic treatment. Additionally, operational aspects such as algal species, temperature, C/N ratio, retention period, and particle size impact biofuel yield. The highest algal biogas yield reported was 740 mL/gVS, subtracted from Taihu de-oiled algae applying thermos-chemical pretreatment under conditions of temperature, time, and catalyst concentration of 70 °C, 3 h, and 6%, respectively. Another high yield of algal-based biogas was obtained from *Laminaria* sp. with mechanical pretreatment under temperature, time, and VS concentration of 38 ± 1 °C, 15 min, and 2.5% respectively, with a maximum yield of 615 ± 7 mL/g VS. Although biofuels derived from algae species are only partially commercialized, the feedstock for biogas might soon be commercially grown. Algae and other plant species that could be cultivated on marginal lands as affordable energy crops with the potential to contribute to the production of biogas are promising and are already being worked on.

1. Introduction

Environmental challenges about the emission of greenhouse gases have driven the hunt for alternative cyclical energy sources. There have been high aspirations for using algae to produce biofuels for a long time [1]. The idea of using algae in biofuel production is

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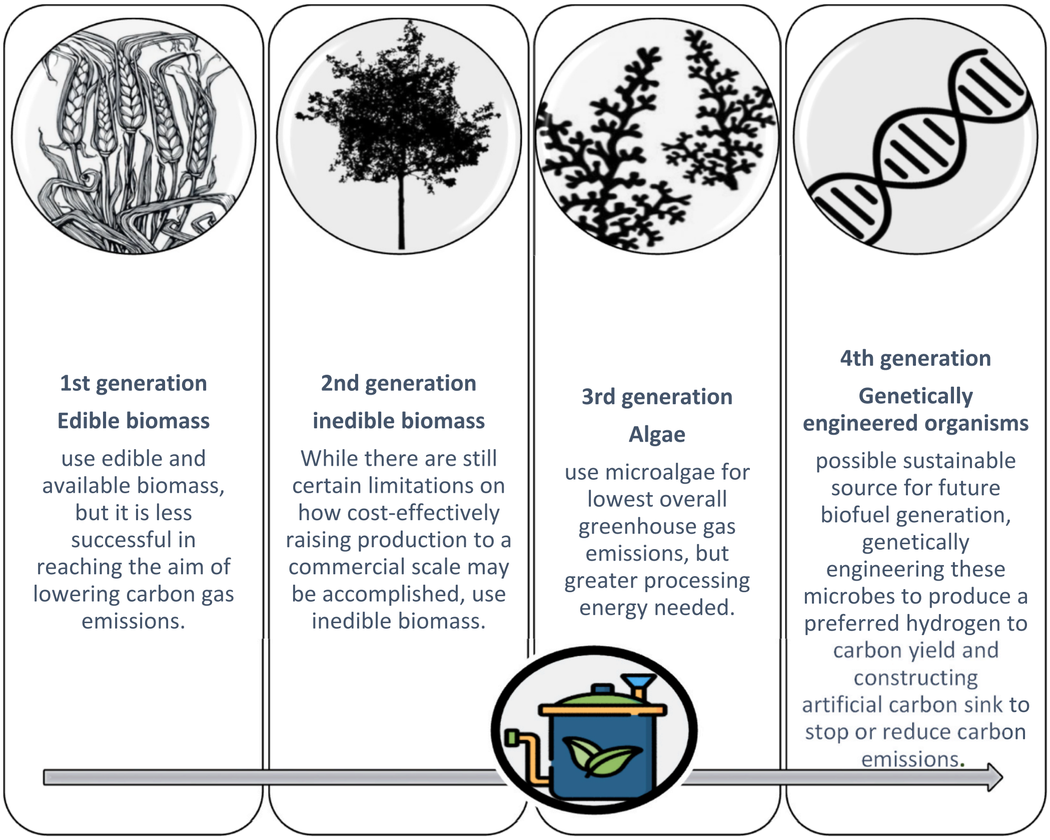

Fig. 1. The four generations of biomass, namely edible, non-edible, algae based and genetically modified organisms, are explained.

less explored due to the challenges associated with commercial cultivation. Biogas production methods are well-known, efficient, and adaptable to a variety of substrates. First, second, third, and fourth generations are the categories used to categorize biofuels in general. Each generation of biofuels attempts to satisfy the world's energy requirements while minimizing negative environmental effects. Sustainability aims to maintain economic progress while safeguarding the environment and meeting human needs [2,3]. Fig. 1 presents the four generations of biomass.

The first-generation biofuels are made from edible biomass including sugarcane and maize, which necessitate exhaustive rural lands to produce enough to trade fossil fuels, resulting in food production rivalry, increasing land clearance, and environmental degradation linked with crop yields and cultivation. The 2nd generation of biomass is based on more efficient renewable substitutes by using inedible lignocellulosic biomass, including switchgrass, sawdust, affordable woods, crop wastes, and municipal wastes; nonetheless, more effort is needed to produce biofuels at competitive costs and quantities [4]. On the other hand, the 3rd and 4th generation feedstock has the capacity to be a long-term biofuel source. More specifically, using algae in biogas production provides a viable option with fewer environmental consequences. However, more research is needed to identify a low-cost method for biofuel production with improved energy efficiency [5]. In order to increase the renewable and sustainable supply of energy, the United Nations has established the Sustainable Development Goals (SDGs). Biofuels or bioenergy are viewed as a promising way to achieve the SDGs by reducing a country's heavy reliance on fossil fuels and fostering an effective resource/waste valuation system and green economy [6]. Algae are a potential renewable biomass source that can substitute for fossil fuels and contribute to the realization of Sustainable Development Goals such as SDG 13 (climate action) and SDG 7 (affordable and clean energy for all) [7,8].

2. Algae-based biogas production

Biogas is a gas that is both combustible and caustic, being produced from any biomass of organic waste, including lignocellulose waste, grass, and leaves wastes, aquatic litter, microorganism waste, domestic solid refuse, and macro-algae. Usually, the composition of biogas is determined by the biomass used in the AD process as well as its operating conditions including, pH, temperature, pressure, and alkalinity, however, CH_4, CO_2, N_2, H_2, water, and traces of hydrogen sulfide (H_2S) commonly found in biogas [9,10]. Biogas produced from algae wastes is attracting attention due to a high proportion of volatile solids providing large-scale production of renewable energy with a low carbon footprint and environmental impact while being economically viable [11,12]. Of these aquatic wastes, microalgae are a third-generation feedstock in biogas production based on fast-growing unicellular organisms in saline,

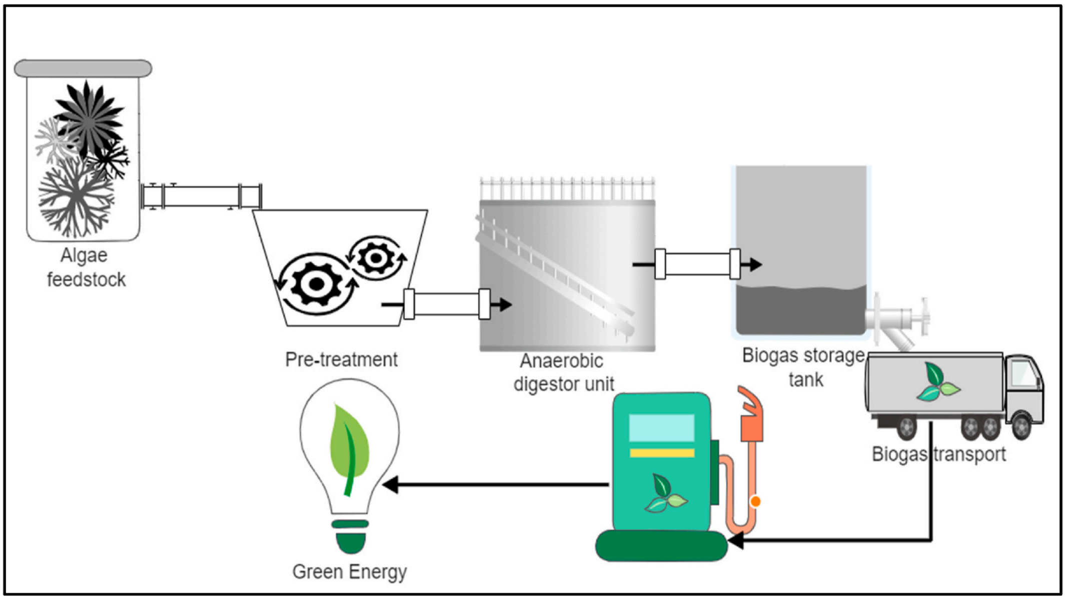

Fig. 2. Algae to biogas production is carried out through pre-treatment, anaerobic digestion, storage, and transportation.

brackish and fresh waters [13]. Microalgae are single-cell photoautotrophic organisms mostly composed of water, that have a high reproduction rate leading to high carbon capture therefore valuable feedstock for biogas production [14]. Microalgae provides a competitive advantage of higher yield per unit area due to their higher rate of growth Microalgae produced in sewage as a culture medium reduces the need for freshwater, and this type of microalgae does not compete and therefore does not affect food crops when grown on uncultivable land [15].

Fig. 2 shows the multiple stages of biogas production using algae including the algae pre-treatment stage and the anaerobic digestion stage starting with anaerobic digestion in the anaerobic unit to create digestate and biogas. CO_2 is introduced into ponds as a source of carbon for the development of algae. While the oil made from algae is transesterified using syngas to provide the necessary methanol, the algae need CO_2 to flourish. The anaerobic digester (bioreactor) uses microorganisms to break down sludge or manure in the absence of oxygen. Continuous, parallel processes like hydrolysis, acidogenesis, acetogenesis, and methanogenesis convert the initial material (carbohydrates, lipids, and proteins) into carbon dioxide and methane gases [16]. For the efficient transformation of the biomass that will enhance the production of bioenergy, just before the AD step, pretreatment of the starting material is carried out, which encourages the cellulosic biomass to produce large quantities of cellulose, converting it through enzymatic processes into carbohydrate polymers fermentable sugars [17]. As a result of the carbohydrates, lipids, and protein found in algal biomass, which undergo breakdown into carbon dioxide and methane to produce high-quality fertilizer and methane-rich biogas, lignocellulosic substrates have a restricted potential to biodegrade [18–20]. As an effective remedy for the world's energy crisis, biogas has demonstrated considerable potential as a renewable energy source for both private and industrial applications. Using biomass resources as a renewable feedstock for the production of power, gasoline, chemicals, and hydrogen has grown in popularity due to growing environmental and policy concerns about pollution and global warming. The production of biofuels, thermal applications like lighting, heating, and cooking, as well as power generation, are the main uses of biogas. Each year, more than 7000 Megawatts of electrical power are generated using biogas [21].

3. Anaerobic digestion

One of the most intriguing approaches for producing biogas is the anaerobic digestion of algae like seaweed, which is also utilized for wastewater treatment [22–24]. The organic component of biomass, which includes plants, algae, and other microbes, may be converted into biogas, a mixture of CH4 and CO2, through anaerobic digestion (AD). Also produced during the process is digestate, a useful organic fertilizer that can take the place of artificial fertilizers in sustainable agriculture. Anaerobic digestion offers a better method for valorizing wet material with high moisture content, such as algae. Bacteria transform organic substrates into a variety of gases through a series of processes known as anaerobic digestion (AD), that take place without the presence of oxygen. It mostly consists of the gases carbon dioxide (CO2) and methane (CH4), with very small amounts of oxygen (O2), nitrogen (N), ammonia (NH3), halogenated hydrocarbons, siloxanes, and hydrogen sulfide (H2S). Fig. 3 depicts the reactions that take place in each of the conversational phases, including hydrolysis, acidogenesis, acetogenesis, and methanogenesis [25–27].

The anaerobic breakdown activates a number of specialized bacteria to form methane gas, CO_2, water, hydrogen sulfide, and ammonia [28]. In addition to the biogas CO2, microalgae enable the simultaneous bioremediation of digestate and the nutrient-rich liquid digestate that results from anaerobic digestion. The use of microalgae to recover nitrogen from AD effluent and upgrade biogas

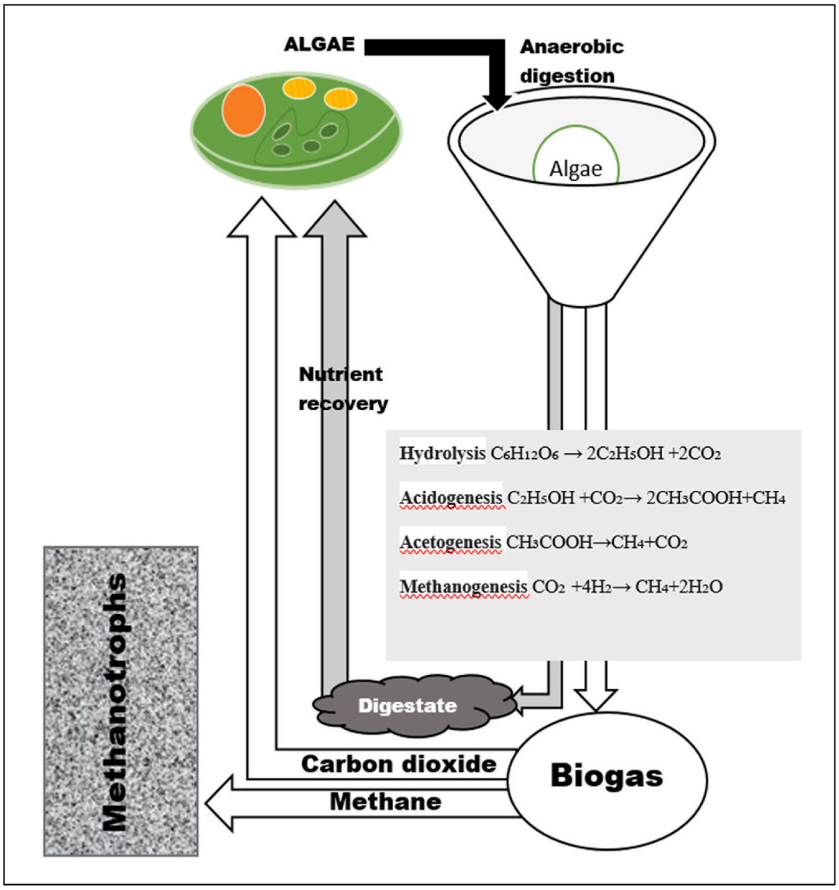

Fig. 3. Anaerobic digestion of algae.

has recently attracted more study attention. Studies have shown that co-cultivating bacteria and microalgae can produce biomass more effectively and eliminate more nutrients than microalgae grown separately [29]. The metabolism of different microbes simultaneously restricts each other in the process, resulting in a complex ecosystem. The best strategy to maximize an anaerobic digestion process is to choose critical operation parameters [30–32]. Unwanted sulfide generation, overly salinity, and the existence of lignin components can all have a negative impact on the rate at which algae biogas is produced. However, by utilizing a range of pretreatment methods such as mechanical, thermal, microwave, enzymatic, and catalytic irradiation, the rate of biogas production can be boosted [33]. Current research focuses on using microalgae to improve biogas made from swine wastewater treated with AD. It has been demonstrated that microalgae remove more than 99% of H_2S from biogas and proved that microalgae removal of CO_2 and H_2S is a potential technique for biogas upgrading [29].

4. Pretreatment of algae for biogas production

Pretreatment is performed by a variety of techniques including mechanical techniques, ultrasound methods, thermal methods, microwave methods, and combined methods; although it is a costly and energy-draining process, it is important to improve the solubility of the biomass and break down its cell wall, which helps to obtain the internal components such as lipids and proteins from microalgae. Different techniques, including mechanical, thermal, ultrasonic, microwave, and hybrid methods used for pretreatment. Pretreatment of microalgae increases bioenergy productivity rate while shortening the processing time and improving the final absorbed substance quality. The purpose of microalgae pretreatment is to release the simpler proteins and lipids by removing the cell wall's complex polysaccharides and converting them into simple monomers. Several variables significantly reduce or even prevent the formation of biogas in microalgae-mediated processes through methane digestion. Lack of Carbon to Nitrogen ratio in the digested feedstock is one of the limiting factors together with cellulose and hemicellulose being harmful to anaerobic bacteria [34]. Nevertheless, polymer organic components such as cell walls, polyphenols, cellulosic fibers, and lignin have lower biodegradability, due to low bacterial efficiency alleviated through hydrolysis improving algal solubility [35,36]. The selection of pretreatment methods is determined by the chemical composition of the algae, as using low-energy processing techniques results in lower yield, the process' energy balance has to be positive for it to have a practical impact [37]. The choice of the pretreatment method is mainly determined by the cost of operation.

4.1. Mechanical methods

For microalgal biomass, mechanical pretreatment comprises physical techniques including milling that aim to reduce size or rupture cell walls by inflicting physical damage (ultrasound, microwave). The cavitation created by soundwave pretreatment causes the cell wall to rupture resulting in broken hydrogen bonds in macromolecules, altering their structures though not all chemical bonds are broken [38].

Mechanical pretreatment, using blades, knives, and hammers increases biogas production by converting net lignocellulose biomass, without generating any hazardous side streams, and is thus suitable for industrial applications [39,40]. The ultimate size of particles was between one and 2 mm, and the most popular techniques involved cutting and chopping. Cell lysis and the dissolution of the polymeric network are brought about by the heat produced by the motion of polar molecules throughout microwave pretreatment. Additionally, the ultrasonic technique generates pressure waves that stir up the solution and cause hydromechanical shear stresses that change the biosolid's structural makeup [41–43]. Pretreatment makes the breakdown of microorganisms and enzymes easier in anaerobic digestion, and it operates without the use of chemical or enzymatic additives, resulting in higher energy dissipation rates and specialized equipment costs increasing capital and operating costs [44,45]. Both microwave and ultrasound techniques are mechanical treatments, and the effectiveness of microwave (MW) pretreatment is contingent upon the density of biomass used, radiation level, and biochemical composition of the substrate. These methods offer better heating efficiency due to direct contact with walls resulting in hydrogen bond breaks [46]. Even though electrical power is transformed to heat equally in the feedstock, it necessitates a considerable energy input, high irradiation power, and a lengthy exposure period [40]. Ultrasound is less efficient at producing methane from the microalgae Monoraphidium sp. and Stigeoclonium sp. than mechanical and thermal pretreatments for AD. Despite making up the majority of biomass and the cell wall, proteins, and carbohydrates were more soluble. There was a linear association between the input of energy and the amount of soluble chemical oxygen demand (sCOD) discharged when the input of ultrasonic energy was increased for S. obliquus and C. sorokiniana. The chosen microalgal strain, the properties of the cell walls, and the total cost and energy needs of the AD process are the factors influencing the effectiveness and use of the ultrasound pre-treatment approach. It is reported that ultrasonography for large-scale biogas production is a feasible method and could offer better efficiency of pre-treatment in terms of cell wall disintegration. When a substrate has significant fiber content and poor degradability, mechanical pretreatment breaks it up, which boosts biogas production and speeds up decomposition [47].

4.2. Enzymatic and catalytic methods

Enzymes operate as catalysts and speed up chemical reactions without changing the balance of the reaction and are frequently found as proteins in nature [48]. Enzymatic pretreatment has been successful in breaking down cell walls, releasing soluble organic substances for processing, and enhancing biogas generation during AD [49]. Cellulase, -amylase, -glucosidase, endo-xylanase, marginal laccase, laccase peroxidase, and manganese peroxidase are popular enzymatic pre-treatment options used while, these enzymes disassemble both cellulose and hemicellulose's polymeric structures, resulting in the byproducts cellobiose, glucose, arabinose, and xylose [50]. The primary benefit of enzymatic pre-treatment is its targeted impact on holocellulose de-polymerization without any sugar loss. In addition, the DF stage of hydrogen synthesis is a bacterial pre-treatment for methanogenesis. Similar bacteria that are involved in AD activities also generate byproducts during DF, including VFAs, ethanol, and lactic acids [51,52]. Enzymatic pretreatment of algal biomass requires a large investment on an industrial scale, and the ideal solution is to find microorganisms that overexpress enzyme-coding genes [53].

Due to minimal energy-draining, high yield of fermented sugars released from biomass under mild operating set-up, lack of eroding problems, and few by-products created, pretreatment with enzymes are considered an eco-friendly procedure. It is possible to differentiate between two categories of enzyme processors based on the origin of the enzymes, which are categorized to be either endogenous enzymes or commercialized exogenous enzymes. The process could suffer from the cost of commercial enzyme manufacturing [54] and combining sonication and enzymatic treatments were more effective than the enzymatic one singly in breaking the cell wall of S. quadricauda [55]. Nanoparticle N-fibers, N-tubes, and N-sheets are applied in the bioenergy sector to increase the efficiency of catalysis and the modification of feedstock enhancing reaction kinetics by enhancing the catalytic activity of microorganisms [56,57]. In addition, it helps to dissolve raw materials, chemical alteration of organic compounds, and release bio-polymeric components such as carbohydrates and proteins [58,59].

4.3. Thermal methods

Thermal pretreatment is essential to dissolve the substrate cytomembrane, accelerating hydrolysis processes and biogas output [60]. Thermal pretreatment procedures effectively damage algal cells while using less energy. In order to dissolve the hydrogen bonds that keep the biomass's mechanical strength, the temperature is applied to its surfaces by heat exchange during heat treatment, which increases the production of biogas. Temperatures exceeding the ideal range, however, tend to be corrosive and accelerate the production of inhibitory compounds, which lowers the efficiency of bioconversion [61,62]. The hydrothermal method is a type of thermal pretreatment that could also remove a higher proportion of hemicellulose and a specific amount of lignin from lignocellulose materials by decomposing them into soluble fractions while also alienating the resistant arrangement [63]. Pyrolysis is the thermal decomposition of biomass in an inert environment at a high-temperature range of 400–600 °C. Pyrolysis of algal biomass has yielded consistent and favorable results in contrast to other conversion techniques, which may lead to their commercialization [64]. Biomass is heated at temperatures below 100 °C during the thermal process, while it requires higher temperatures in hydrothermal pretreatment followed by an increase in pressure. A positive association exists between biomass solubilization affected by temperature and time and methane yield, with temperature sometimes having a greater impact on thermal pretreatment [65].

Table 1 shows the yields using different pretreatment methods, Chlorella minutissima microalgae and Ulva lactuca macroalgae oil waste was used to explore the impact of temperature and the size of particle parameters on biogas formation. One of the most common seaweeds in Turkey is U. lactuca macroalga, and it has considerable potential for waste. Since C. minutissima oil content is suitable for generating biogas, it is widely cultivated; nevertheless, the extraction process produces a lot of waste. During 30-day retention period, a 1:4 W/W alga to inoculum ratio and at 55 °C, the maximum biogas yield for Ulva lactuca macro-algae achieved was 342.59 cm^3/g VS. The maximum biogas obtained was 341.43 cm^3/g VS for O-E *Chlorella minutissima* microalgae. This quicker biomass hydrolysis induced by the lower particle size that is because hydrolysis enzymes can more easily attach to substrates [11]. Algal biomass *Enteromorpha* underwent pretreatment using Co NPs + MW. The maximum total biogas generation, 53.60 mL/g TS, was achieved at 6 min, 600 W, and 1 mg/L of cobalt (Co) NPs. Anaerobic digestion was performed in batches for 264 h. This study reported that microwave pretreatment begins early in green algae hydrolysis with a reduced lag time. NPs had a positive effect on biogas output during the last stages of anaerobic digestion [58].

Laminaria sp. and *Ascophyllum nodosum*, two native Irish seaweeds, examined as potential feedstock for the AD process used to produce methane. Laminaria sp. is shown to be more suited for biogas conversion than Ascophyllum nodosum, according to the data, which also showed that methane yields had generally increased by 40%. The RSM analysis showed that, in comparison to the pretreatment period, the VS concentration significantly affected the methane production of both species. The research indicated that Laminaria sp. and Ascophyllum nodosum produce the most biogas, at rates of 615 7 $\frac{ml}{g}$ VS and 402 $\frac{ml}{g}$ VS, respectively. These yields were reached at 2.5% VS and 1% VS, and by extending the beating time to 15 min [66]. Generally, ultrasound and microwave pretreatment are more effective than untreated biomass at increasing biomass solubilization and methane output when higher specific power or longer exposition times are used.

The green microalgae help to produce methane when exposed to metal oxide nanoparticles. A research study has reported, 500 mL, 37 °C, 150 rpm mixing rate, and 170 h of hydraulic retention time are the ideal operation settings for anaerobic digestion at a concentration of 10 $\frac{ml}{g}$ of Fe3O4 NPs. According to the findings, NPs have a moderately good impact on biogas production up to 60 h of residence time but thereafter dramatically improves. Fe_3O_4 NPs were able to produce a total biogas output of up to 624 mL, and their overall biogas production increase was 28% [71]. Results indicated that this pretreatment combination generated more biopolymer compounds, which led to more biogas than other pretreatment combinations while also dramatically reducing the lag period. Less than 37 °C, the highest biogas output was determined to be 362 mL, and the mixing speed was around 150 rpm. Pretreatment with a microwave for 210 s at 800 Watt and 10 $\frac{mg}{L}$ dosages of Fe_3O_4 [72]. The highest yield of 81.8 $\frac{L\ CH_4}{Kg}$ VS for Fucus vesiculosus was obtained by mechanical pretreatment and salt washing combination. Under the same conditions, Ulva intestinalis produced 92.100 $\frac{L\ CH_4}{Kg}$ VS. Without the usage of any other factors, Cerathophyllum demersum produced the most CH4 at a rate of 405.3 $\frac{L}{Kg}$ VS. Each alga responds differently to washing and mechanical pre-treatment. While washing generally improves conditions +25 $\frac{L\ CH_4}{Kg}$ VS, mechanical pretreatment only has beneficial results for marine algae +35 $\frac{L\ CH_4}{Kg}$ VS. Compared to freshwater algae, the proportionate effect is greater for marine algae because their cell walls are stronger and harder for bacteria to break down, requiring less mechanical pre-treatment [75].

The pretreatments are done on Luminaria spp. show that mechanical pretreatment yields more biogas from the microalgae than microwave pretreatment (Table 1). In fact, a study of the pre-treatments of Laminaria spp. using milling, microwave, and beating found that beating was the pre-treatment that produced the greatest net energy gain and was superior to drying before ball milling [80]. Another microalgae species used in multiple studies is Enteromorpha microalgae that went under the microwave pretreatment method combined with nanoparticles such as iron oxide and magnesium oxide and results showed enhanced biogas yields than normal microwave pretreatment method.

5. Factors affecting biogas production from algae

Production of biogas can be influenced by factors such as the C/N ratio, particle size, time, temperature, algae species, and seasonal changes, while the amount and quality of the finished product are influenced by the temperature of the reaction, heating rate, and supply of oxygen during anaerobic digestion [81].

5.1. Carbon-to-Nitrogen ratio and particle size

Carbon to nitrogen ratio is a sign of nutritional imbalance: A poor ratio of C/N suggests that the feedstock contains a lot of nitrogen, resulting in the release of ammonia during protein hydrolysis, whereas a high C/N ratio may lead to VFA buildup. Because algal biomass has a poor ratio of C/N, it may impede methane output because it is unsuitable for anaerobic digestion. However, Co-digestion of algae with carbon-rich wastes is used to alleviate this problem successfully to create a high C/N ratio and increase methane output by lowering ammonia levels below inhibitory [82]. Since acidogenic bacteria consume nitrogen more quickly than methanogenic bacteria, a high C/N ratio prevents biogas generation from reaching its maximum potential. For increased biogas conversion, bacteria need a carbon-to-nitrogen ratio between 20 and 30, as they eat carbon at a rate 30 times faster than they do nitrogen [83]. The fundamental impact of lowering the particle size of the substrate is that anaerobic microbes have easier access to organic materials. Moreover, the lignocellulosic material's smaller particle size lessens the chances of the creation of a floating layer, which reduces the

Table 1
Comparison of yields from different pretreatment methods of algae biomass and their operating conditions.

No.	Species	Parameter and conditions	Yield	Ref.
1	*Ulvalactuca* macroalgae	Temp:55 °C Time:30 days Particle size:200 μm Alga–inoculum ratio:1:4 (g:g)	342.59 $\frac{cm^3}{g}$ VS	[11]
2	*O-E Chlorella minutissima microalgae*	Temp:55 °C Time:30 day	341.43 $\frac{cm^3}{g}$ VS	[11]
3	*Laminaria* sp.	Temp: 38 ± 1 °C Time:15 min VS:2.5% Mechanical Pretreatment	615 ± 7 $\frac{ml}{g}$ VS	[66]
4	*Ascophyllum nodosum*	Temp: 38 ± 1 °C. Time:15 min VS:1% Mechanical Pretreatment	402 ± 20 $\frac{ml}{g}$ VS	[66]
5	*Enteromorpha*	Power:656.92 W Time:5.10 min Liquid-solid ratio: 33.63:1 Microwave pretreatment	Biogas 244 $\frac{ml}{g}$ VS	[31]
6	Taihu de-oiled algae	Temp:70 °C Time:3 h Sodium hydroxide concentration: 6% Thermo-chemical pretreatment	740 $\frac{ml}{g}$ VS	[67]
7	*P. canaliculata*	F/I value: 0.3 Time: 50 min Mechanical pretreatment	283 $\frac{ml\ CH_4}{g}$ VS	[68]
8	*Laminaria* sp.	Temp:38 ± 1 °C Time: 25 days Microwave pretreatment	244 $\frac{ml\ CH_4}{g}$ VS	[69]
9	Mexican Caribbean macroalgae	Biological pretreatment	104 $\frac{ml\ CH_4}{g}$ VS	[70]
10	Enteromorpha	Power of 600 W Slurry liquid: solid ratio: 20:1 Time: 6mins Microwave co-treatment	53.60 $\frac{ml}{g}$ Ts	[58]
11	*Chlorella* sp.	Temp: 37 °C Time: 60 h Biological pretreatment	415.6 $\frac{ml\ CH_4}{g}$ VS	[71]
12	*Enteromorpha*	Temp: 37C Time: 170 h, Fe3O4:10 mg/L Chemical pretreatment	624 mL biogas	[59]
13	*Enteromorpha*	Temp: 37 °C, Mixing speed: 150 rpm Time:3.5 min Power: 800 W Fe3O4:10 mg/L Microwave pretreatment and nanoparticles pretreatment	362 mL biogas	[72]
14	*Ulva lactuca*	Ozone dose: 249 mg O_3 g^{-1}VS Time: 15 min Ozonation Pretreatment	498.75 mL/g VS	[73]
15	*Scenedesmussp.*	Temp:75 °C Time:10 h Thermal pretreatment	339 $\frac{ml\ CH_4}{g}$ VS)	[74]
16	Saccorhiza polyschides	Temp: 37 °C Time: 53 days Stirring speed: 80 rpm TS:2.5%	146 ± 2 $\frac{ml}{g}$ VS	[75]
17	*Fucus vesiculosus*	Temp: 37 °C Time: 5 days Mechanical pretreatment and washing of salt	81.8 $\frac{L\ CH_4}{Kg}$ VS	[75]
18	*Ulva intestinalis*	Temp: 37 °C Time: 5 days Mechanical pretreatment and washing of salt	92.1 $\frac{L\ CH_4}{Kg}$ VS	[75]
19	Red Algae *Pterocladia capillacea*	α-Fe_2O_3: 10 mg/L Time: 40 days	219 $\frac{ml}{g}$ VS	[76]
20	*Cerathophyllum demersum*	Temp: 37 °C Time: 5 days No pretreatment	(405.3 $\frac{L\ CH_4}{Kg}$ VS	[77]
21	Sargassum fulvellum	Particle size: 75–850 μm Mechanical pretreatment	142.91 ± 0.004 $\frac{ml\ CH_4}{g}$ VS	[78]
22	*Chlorella*pyrenoidosa	15 min, 121 °C, and 15 psi of pressure. Hydrothermal pretreatment	493.19 $\frac{ml}{g}$ VS	[79]

reactor's methane outflow [84]. The amount of energy required for lignocellulosic material size correlates with biomass type and moisture content. Lignocellulosic materials' size reduction during milling pretreatment increased the anaerobic digestion's capacity to buffer, which helps to reduce the acidity of AD. The substrate's particle sizes have an immediate impact on digestion since they immediately correlate with the amount of hydrolysing enzyme surface area that is accessible [85,86].

5.2. Retention time and temperature

In order to build and improve anaerobic digestion systems, retention time is a crucial factor. Retention time (RT) is referred to by both hydraulic retention time (HRT) and solid retention time (SRT). Microalgae with thick cellular walls have improved Anaerobic Digestion when retention time stimulation is applied. The influence of RT can be determined by analyzing pretreated microalgae AD acquired at different periods. In general, increasing the RT increases methane yield thus enhancing biogas production of pretreatment microalgae [74,87]. Thus, even if pretreatments are used, operating microalgae digesters at modest RTs appears more suitable, the pretreatments simply damage the cell wall of the microalgae without entirely releasing all cell's internal substances. Reactors running at a longer RT require a balance between energy needs and gains during the pretreatment step as well as expansion in volume, surface area, and expenditures [88]. Studies suggest that the optimal habitat for biodegradation ideally ranges between 50 and 60 °C [83]. Other pretreatment temperatures for increased production of methane from microalgal biomass are reported to be between 55 and 170 °C [13], including those that exist within the thermophilic and mesophilic zones. The enhanced heating leads to increased rates of hydrolysis and significant biogas generation. Since microorganisms acclimate to a unique temperature and require new microbial structures to re-adapt to a new temperature, low ranges of temperature change could have a major impact on methane output for a specific operational temperature type.

High temperatures partially hydrolyze macromolecules like proteins, lipids, and carbohydrates as well as solubilize organic materials. They may also encourage the production of molecules that interfere with the metabolism of anaerobic microbes, particularly ammonia. Temperature has a great impact on AD processing steps as temperature conditions for optimizing methanogenic bacteria cultivation, particularly mesophilic methanogen species vary from those that improve hydrolysis or acidification stages [89].

5.3. Algae species and seasonal change

Various environments, including freshwater and sea water, deep oceans, rocky coasts, both closed and open ponds, photobioreactors, sewage and wastewater, the desert, CO_2-producing enterprises, etc., algal development such as that of the Chlorophyta, Rhodophyta, and Phaeophyta families can be found [90]. The choice of microorganisms such as algae for the degradation of organic waste affects the stability of the process as well as the conversion rates. *Genera Ulva (Chlorophyta), Laminaria, Fucus,* and *Saccharina* are among the most extensively studied seaweeds for the generation of biogas. There are still a number of issues that prevent these species from producing biogas, including the seasonal effect on biomass produced, the presence of chemical inhibitors, and the high cost of harvesting. Researchers have used several strategies such as pretreatments, AcoD, and additive supplements, to counteract the inhibitory factors and improve the effectiveness of AD [91].

The algal biomass's suitability for usage as a feedstock for biofuel is determined based on its chemical characterization. For instance, green microalga *Chlamydomonas reinhardtii* has the amazing capacity to hydrolyze water into hydrogen when illuminated, while brown macroalgae has minimal lignin and rich carbohydrate content, is an untapped resource and a promising replacement to standard fossil fuels [61,92]. Recent studies have also highlighted the unique qualities of microalgal biomass extracted utilizing several microwave technologies, including Botryococcus braunii and Chlorella vulgaris. The results of lipid extraction with microwave pretreatment were superior for the former species than for the later species, demonstrating unequivocally that each species favors a certain pretreatment technique [93]. Seasonal changes can greatly alter the chemical makeup of seaweeds, which therefore changes the amount of inhibitory chemicals present. Pretreatment was one method used to lessen the negative effects of inhibitors while increasing the output of biogas. There are still a number of issues with these species' capacity to make biogas, including the effect of seasonal change on biomass output, the existence of inhibitory compounds, and the high cost of harvesting [53,94,95].

6. Future perspective

The identification of an environmentally friendly source of transportation fuels is one of the largest challenges in recent years. Due to the production of biofuels using feedstock obtained from the exploitation of arable land, difficulties such as rising food prices and shortages may arise. Algae are a neutral alternative to traditional agricultural raw materials that can be found close to water basins and used as a raw material to create biogas. As algal growth is the seasonal, sustainable method to produce energy from algal biomass requires artificial open tanks or photobioreactors [96]. The possibility of microalgae production to reduce GHG emissions while simultaneously providing value-added bioproducts like biogas has increased its industry's appeal in recent years. It is necessary to conduct more research on the method of turning digestates into a solid or semi-solid form, that has less volume than liquid digestate and can be utilized in a variety of downstream applications, including bio-fertilizers. However, integrating clean technologies like anaerobic digestion and microalgae production is necessary to concentrate and recover nutrients from fertilizers, reuse all components of manure, and extract additional value [97,98]. Additionally, this process captures CO_2 while creating biomass, that can then be transformed into biofuels or products with added value, helping to reduce global warming. Microalgae use 1800 g CO_2 in order to create 1 kg of biomass thereby sequestering carbon dioxide and microalgae technology is regarded as an important tool in upgrading systems in biogas production. Therefore, it renders it a resource that has promise for both addressing environmental and energy-related

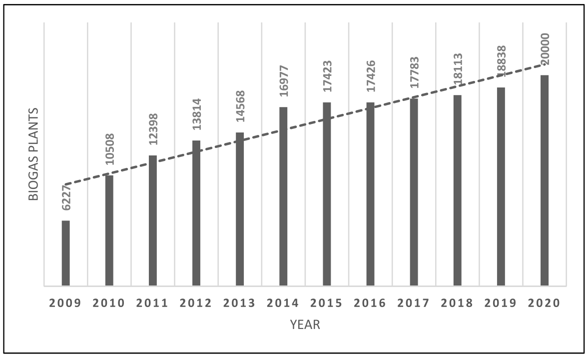

Fig. 4. Europe's biogas facilities development (2009–2020) [101].

problems. Microalgae also have a number of notable advantages over other energy crops, including better photosynthetic efficiency, a lower water use demand, and the absence of an arable land requirement [10,99,100].

The reported biogas and biomethane production can nearly double by 2030 and more than quadruple by 2050. The EBA Statistical Report 2020 demonstrates tremendous growth of biomethane and promises to decarbonize the gas industry. This shows that biogas and biomethane can have a considerable impact on the de-carbonization of the fuel industry by enabling the use of renewable gases for heating, industry, and transportation [101]. Based on EBA research, Fig. 4 shows the growth in the number of biogas facilities in Europe between 2009 and 2020 [102]. The need to discover suitable biomass that can support the large-scale production of biogas is brought on by the expectation that this expansion will continuously grow over the next years [101,102].

Research and development are ongoing for the commercialization of lab-scale microalgae growth for the production of biogas. Due to limitations such as variation selection for higher biomass output, selection of the microalgae growth system, quality, and quantity of bio-based recycled and recovered from algae, operational variables, and other external factors. On the other hand, there are challenges that deter the use of biofuels derived from algae species and make it only partially commercialized such as the high cost of production and the restrictions on growing, harvesting, and processing. Biogas is abundantly found in large quantities in places like landfills, sewage treatment plants, and animal and agricultural waste. As a result, efforts are already being made to diversify cheap energy crops, such as algae and other plant species that can be grown on marginal land to contribute to the production of biogas [96,103].

7. Conclusions

This review article has highlighted the best operating conditions for high biogas yield from algae and the optimal operating conditions. Traditional fuel consumption and production emit large amounts of CO_2 and other greenhouse gases resulting in global warming. Algae has a greater energy potential than biomass or solid waste from municipalities and the potential to be a commercially viable aquatic energy crop. The highest algal biogas yield reported was from de-oiled algae applying thermos-chemical pretreatment under fixed conditions of temperature, time, and catalyst concentration. The high yield of algal-based biogas obtained from *Laminaria* sp. with mechanical pretreatment has shown significant promise. Based on the data reviewed, it has been found that mechanical pretreatment of the microalgae produces more biogas than microwave pretreatment. A comparison of Laminaria spp. pre-treatments employing beating, milling, and microwave technology revealed that beating produced the greatest net energy gain and was superior to drying before ball milling. According to studies, pretreatment of Enteromorpha using a microwave technique in combination with nanoparticles like iron oxide and magnesium oxide increased biogas production over conventional microwave pretreatment. Both time and temperature, influence biomass solubilization with temperature having a stronger influence on thermal pretreatment. It is important to take into consideration that there are factors affecting biogas production such as C/N ratio and particle size, temperature and time, and species and seasonal change. Related studies have revealed that pretreatment temperatures should decrease between 55 and 170 °C to boost the production of methane from microalgal biomass. Some studies suggested that the ideal habitat for biodegradation is at warmer temperatures, it ideally ranges between 50 and 60 °C, while the ratio of C/N must be kept between 20 and 30 for improved biogas conversion. Biogas and biomethane have the potential to contribute to the decarbonization of the gas industry by permitting the use of renewable gases for heating, industry, and transportation. As a result, the output of algae-based biogas is likely to increase greatly in the next years. Future research should focus on technical advancement and efficient algal strain screening, as well as their application, which are vital for productive research and development.

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