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INVITED REVIEW PAPER

Overview of anaerobic digestion process for biofuels production from marine macroalgae: A developmental perspective on brown algae

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Abstract−Meeting renewable energy policies (such as Renewable Portfolio Standard, RPS and Renewable Fuels Standard, RFS) requires development of a large sustainable biomass resource; macroalgae could be a potential contributor towards this policy to produce biofuels. In particular, massive brown algae have been considered a promising biomass to accomplish the biofuel goals in the nearest future. The most direct route to producing biofuels from brown algae is via anaerobic digestion (AD) process. Although the application of brown algae for AD process is still at an early stage, there is almost no technical barrier to the process, particularly as an additional feedstock for existing AD may contribute to the fast development of industrial biofuel application. This review provides an overall perspective required for an advanced assessment of the development of brown algae as a sustainable biofuel resource from the AD process.

Keywords: Anaerobic Digestion Process, Biofuels, Biomethane, Brown Algae, Volatile Fatty Acids

INTRODUCTION

Meeting renewable energy goals to substitute fossil fuels and to prevent the emission of greenhouse gases requires development of sustainable and environmentally friendly resources; attention is focusing to the use of carbon-neutral biomass. Biomass is biological material derived from living things that most often refers to plants or plant-based materials [1] which survive through the process of photosynthesis to convert solar energy into the chemical energy. This biomass can be converted inside chemical carbon energy into biofuels, such as bioalcohols (i.e., bioethanol [2-4], biobutanol [5-7], and mixed alcohols [8,9]), bio-oil [10-12], biodiesel [13-15] and biogas (i.e., biohydrogen [1,16-18] and biomethane [19,20]). Namely, the term 'biofuels' has come to mean the conversion of biomass to provide the energy for substituted transport fuels [21].

Attention is currently turning to the use of marine biomass (i.e., macro- and micro-algae) to supplement land plants (i.e., energy crops and lignocellulosic biomass) as a source of feedstock for sustainable biofuels production. In particular, macroalgae (green-, red-, and brown algae), commonly referred to as seaweeds are intensively considered as attractive renewable resources with many advantages over land plants: a growth rate with high productivity, greater potential for carbon dioxide fixation, and abundant content of carbohydrates which are easily converted to biofuels [22,23]. Also, macroalgae have less lignin content and have no drawbacks of high lignin content requiring cost- and energy-intensive pretreatments to depolymerize compared with lignocellulosic biomass [24]. Consequently, the use of macroalgae is more convenient for producing biofuels, and several pioneering studies of biofuels production have been initiated.

In particular, biogas production with intermediated organic acids is the most direct route to producing biofuels from macroalgae via anaerobic digestion (AD) [25]. One successful large-scale study of biogas production derived from AD of brown algae [26] could be only realized that massive brown algae have been considered as a promising biomass to accomplish the biofuel goals in the nearest future. In this perspective, this review provides an overall perspective on AD process required for an assessment of the development of brown algae as a sustainable biofuels resource. Also, the integrated AD platform including several cost-effective strategies desired for an initial evaluation of large scale is discussed.

BROWN ALGAE AS BIOFUELS FEEDSTOCK

Marine macroalgae, which refers to seaweeds, are eukaryotic photosynthetic marine organisms classified as green algae (*Chlorophyceae*), red algae (*Rhodophyceae*) and brown algae (*Phaeophyceae*) defined by their phytopigments [27]. They are abundant in the world's coastal waters and diverse, with 1,500, 6,000, and 1,800 species of green-, red-, and brown-algae, respectively [28]. These macroalgae are rich in carbohydrates; fermentable sugars may be obtained for producing biofuels production.

To get higher biofuel yields from macroalgae, strategies under consideration need all potential sources of feedstock to meet the biofuel production goals. The most dependable component, chemical composition of macroalgae as a feedstock, directly affects the performance of biofuel yield. Therefore, an understanding of their chemical types and available content in macroalgal biomass is essential for developing the biofuel process [29]. Also, another key factor which in many cases originally determines the high mass produc-

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‡This article is dedicated to Prof. Hwayong Kim on the occasion of his retirement from Seoul National Univerisity.

Table 1. Chemical condition and growth information of representative macroalgae species

Classification	Component	Unit	Green algae	Red algae	Brown algae	References
Representative species			*Ulva*, *Codium*	*Gelidum*, *Gracilaria*	*Saccharina*, *Sargassum*	[6,7]
Chemical composition	Water	% of wet	70-85	70-80	79-90	[60,92]
	Minerals	ash, % of dry	10-25	25-35	30-50	[60,92]
	Carbohydrates	% of dry	25-50	30-60	30-50	[16,29,33,58,60,92]
	major component		Starch	Agar	Alginate (~≤40)	
	Cellulose	% of dry	20-40	2-10	2-10	[60,92]
	Proteins	% of dry	10-15	7-15	7-15	[60,92]
	Lipids	% of dry	1-2	1-5	2-5	[60,92]
Growth conditions	Water temperature	°C	10-25.5	15-25	10-15	[47,93,94]
	Light intensity (Irradiance)	μmol/m^2/sec	88.5	25-75	30	[93-95]
Growth rate		%/d	8.04	1-3.5	7-16	[93,95]
Production regions			Philippines, Vietnam, China, Republic of Korea	Philippines, Vietnam, China, Japan, Republic of Korea	China, Japan, Republic of Korea, Japan	[29,46]

tion of macroalgae utilization for biofuels production is the selection of their species. Indeed, the areal productivity (ton/ha) of brown algae is significantly higher than green- and red-algae. The large brown algae, kelp, for instance, can grow as fast as half a meter a day, ultimately reaching 30 to 80 meters [30]. Therefore, this promising biomass, brown algae, has been considered economically feasible for sustainable biofuel production.

The representative species of *Ulva*, *Codium* for green-, *Gelidum*, *Gracilaria* for red-, and *Saccharina*, *Sargassum* for brown-algae have been applied to biofuel production [29-31]. The chemical composition information regarding growth conditions (water temperature and light intensity for photosynthesis), growth rate, and major production region of representative macroalgae is listed in Table 1. Green- and red-algae are attracting interest as a resource of bioalcohols (bioethanol and biobutanol) [3] due to the comparatively high level of accessible fermenting sugars (starch and agar; Table 1), while fermentative biofuel production from the main carbohydrate in brown algae (alginate) is limited primarily by the availability of tractable microorganisms that can metabolize alginate polysaccharide [24].

Alginate is a principal material of the cell wall [32,33] that accounts for up to 40% dry wt. in brown algae and has a chemical structure that consists of two uronic acids (manuronic acid and gulonic acid) each containing a carboxyl group [23,34]. Because alginate maintains its carboxylic group structure during the degradation, a high yield of organic acids can be theoretically available from alginate by AD rather than bioalcohol production by fermentation [22,35]. Therefore, alginate decomposition by anaerobic microorganisms can be realized to convert to biofuels such as organic acids and methane during the AD process. From this standpoint, the early efforts of AD processes from brown algae and alginate to produce volatile fatty acids (VFAs) and biomethane have demonstrated the efficient feasibility of AD for conversion of brown algae to biofuels [22,23,31,36].

ANAEROBIC DIGESTION PROCESS FOR BROWN ALGAL BIOFUELS

AD is a series of biological processes combined with hydroly-

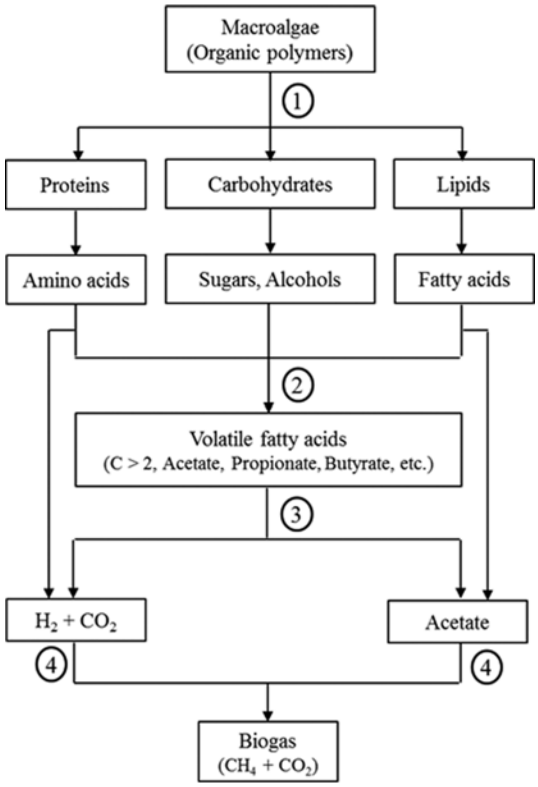

Fig. 1. Process pathway of the degradation of macroalgae by anaerobic digestion.
① Hydrolysis ③ Acetogenesis
② Acidogenesis ④ Methanogenesis

sis, acidogenesis, acetogenesis, and methanogenesis converting wet organic feedstock (10-15% dry matter) into intermediated VFAs and methane (Fig. 1) under little or no oxygen condition by different types of microorganisms [37-40]. The process of AD is a well agreed, less complicated and comparatively low cost technology for generating biofuels as biomethane and VFAs [38,41]. AD of brown algae is a prospective feasible option for producing renewable energy sources for industrial urgent demands [42]. Here, we present the applicability of brown algae for VFAs and biomethane productions reported to determine the effectiveness of anaerobic biofuels process, including preprocessing before the direct conversion.

1. Preprocessing

Preprocessing of raw brown algae includes the debris screening, storage and transport from the harvesting site on mechanical processing [43] before the downstream conversion processes. Debris such as stones, snails on the surface of the brown algae, and garbage must be removed for all applications, especially for the next mechanical processing (chopping and milling) [30,44,45].

Mechanical processing is used to reduce brown algae to particle sizes more efficiently processed [46] to obtain both reducing of the particle size and increasing the specific surface area available to microorganisms [45]. However, even mechanical processing is necessary, and high energy and cost requirements are still a challenge to reducing the maximum feedstock cost. Also, low efficiency of milling caused by slippery gel-like consistency of alginate in cell wall should be considered to develop the equipment design.

After shore farming of brown algae, practically, the moisture content of fresh feedstock must be reduced to less than 20 to 30% [30, 47] in dewatering for transport to the conversion facility of biofuels. However, mechanically processed feedstock can directly transfer into the reaction; thus dewatering is not mandatory as part of the preprocessing phase, in AD or fermentation (a requirement of water to react), while dewatering or drying is essential to dry pyrolysis, which requires biomass with low water content (typically wood or crop residues) for bio-oil production [48]. In this context, AD process from brown algae offers an economic benefit to reduce the energy cost of systems.

Even though the direct conversion of brown algae into AD is feasible, pretreatment is necessary to condition and increase digestibility and degradation rate of brown algae [44,49,50]. Purposes of pretreatment process are to preserve the total organic matter content and to prevent the formation of inhibitory materials [44]. To date, even though little information has been reported to provide efficient solutions for increasing brown algal digestibility in AD process, various pretreatments of physical, chemical, and biological methods of brown algae (particularly alginate) can improve the yields of final products and support the development of a successful AD process.

2. Volatile Fatty Acids

In the AD (Fig. 1), simple organic monomers from hydrolysis are converted into VFAs referred to as short-chain fatty acids (i.e., C2 to C6; acetic acid propionic acid, and butyric acid etc.) from acidogenesis. VFAs are potential feedstock for several biotechnological applications such as biohydrogen [51,52], biomethane [53], biodiesel [54], mixed alcohols [8], and bioelectricity productions through microbial fuel cell [55-57].

Table 2. Maximum volatile fatty acids (VFAs) yield data from macroalgae and their carbohydrate components

Feedstock	VFAs yield (kg carbon in TVFAs/ kg carbon in feedstock)	References
Brown algae		
Saccharina japonica[a]	0.334	[61]
S. japonica[b]	0.638	[23]
Alginate[a,c]	0.371	[36]
Red algae		
Gelidium amansii[a]	0.304	[58]

[a]No pretreatment
[b]Biological pretreatment was performed by *Vibrio* spp.
[c]Alginate is a principal carbohydrate of the cell wall in brown algae accounted for up to 40% dry wt

Even though the AD process has been used in organically loaded waste treatment for over 60 years, VFAs from brown algae have recently been considered as an intermediated feedstock for biofuel production. In Table 2, early efforts demonstrated the feasibility of acidogenesis for conversion of brown algae or their carbohydrate component (alginate) to VFAs [22,23,36,50], but there is only one study for red algae up to now [58]. The VFAs yields of brown algae and alginate ranged from 0.334 to 0.638 kg carbon in TVFAs/kg carbon in feedstock representing a higher value than that of red algae (0.304 kg carbon in TVFAs/kg carbon in feedstock). This suggests that the main carbohydrate (alginate) of brown algae has a potential for economic priority for VFAs production compared to the carbohydrate (agar) of red algae in the AD process.

In a chemical-based industry, VFAs are valuable compounds which are the building blocks of various organic compounds including alcohols, aldehydes, ketones, esters, and olefins and diverse uses in the market [59-61]. The interest in economy prompts the improvement of existing processes and, for VFAs not previously available by acidogenesis, the development for recovering process to use in the market as valuable chemical compounds. Meeting this perspective requires the initial assessment of the recovery of VFAs from brown algae for future technical efforts for advanced AD process. The primary recovery of carboxylic acids from fermentation broths may be carried out via various applied techniques such as liquid-liquid extraction [62,63], adsorption [64-66], precipitation [67-69], ion-exchange [70,71], pertraction [72,73], membrane-based solvent extraction [74-76], and electrodialysis [77-79] listed in Table 3.

Though these technologies can achieve the combined approaches to removing major impurities, water, and minor impurities from acidogenesis, the very different physical properties of various carboxylic acids and process are still a challenge to achieve economic success for recovering VFAs in situ. Therefore, results for direct utilization of VFAs for next biofuels production (biomethane) are encouraging.

3. Biogas

Biogas is typically a mixture of gases which are primarily methane (CH_4) and carbon dioxide (CO_2) with small amounts of hydrogen sulfide (H_2S), ammonia (NH_3), siloxanes, hydrocarbons, oxygen

Table 3. Technologies employed for VFA recovery from the fermentation broth

Recovery technology		Volatile fatty acids	Materials utilized	Reference
Liquid-liquid extraction		TVFA[a]	TOPO[b] in kerosene	[96]
		TVFA[a]	TOPO[b] in dihexyl-ether	[63]
		Acetic acid	TOA[c]/2-ethyl-hexanol	[97]
		Propionic and butyric acid	Aliquat 336/oleyl alcohol	[62]
		Propionic acid	TOA[c]/diluent (hexanol, butyl acetate, and petroleum ether)	[98]
	Amine based	Propionic acid	1-Octanol; Butyl acetate; Hexane	[99]
	Amine based	Acetic acid	MIBK[d], Kerosene (1-octanl)	[100]
	Ionic liquid	Monocarboxylic acid (propionic acid)	Shellsol A	[101]
	Ionic liquid	Propionic acid	Dodecane (1-decanol)	[62]
	Neutral/solvating	Monocarboxylic acid (acetic, propionic, butyric acid)	Hexane	[102]
	Neutral/solvating	Organic acid	Sunflower oil	[103]
	Neutral/solvating	Acetic acid	1-octanol	[100]
	Neutral/solvating	Propionic acid	Hexane	[104]
Membrane based	Liquid-liquid extraction	Acetic acid	TOA[c]/MIBK[d]; octanol; n-alkanes	[75]
		Propionic acid	TOA[c]/xylene	[105]
Membrane based	Liquid-liquid extraction /stripping	Butyric acid	Amines/(corn oil, oleyl alcohol)	[74]
Electrodialysis		Organic acid	Bipolar membranes	[78]
		Organic acid	Anion exchange membranes	[77]
Pertraction	MSH[e]	Acetic and propionic acid	(TOA[c]/TOPO[b]; TBP[f])/hexane	[106]
	BLM[g]	Butyric acid	Puren-alkanes	[72]
Pervaporation		Acetic acid	Zeolite membrane	[107]
Adsorption	Weak anion exchanger	Carboxylic acid (acetic acid)	Polyacrylic (macroporous)	[65]
	Weak anion exchanger	Carboxylic acid (acetic acid)	Poly(4-vinylpyridine)-DVB[h] (macroporous)	[65]
	Strong anion exchanger	Organic acid (acetic, propionic and butyric acid)	Polystyrene-DVB[h] (gel)	[64]

[a]TVFA: total volatile fatty acids
[b]TOPO: trioctylphosphine oxide
[c]TOA: tri-*n*-octylamine
[d]MIBK: methyl isobutyl ketone
[e]MHS: multimembrane hybrid system
[f]TBP: tri-*n*-butylphosphat
[g]BLM: bulk liquid membrane
[h]DVB: divinylbenzene

(O_2), carbon monoxide (CO), nitrogen (N_2) and moisture [80,81] in AD. The methane-rich biogas is a renewable energy that can be substituted to compressed natural gas (CNG) through the upgrading technology [82,83]. The value of biogas to meet renewable energetic demands of the near future has continued to play a role in the formation of energy policy for a number of years, including the recent establishment of the Renewable Portfolio Standard (RPS) and Renewable Fuels Standard (RFS) in developing countries [84].

The biogas process from brown algae can be an alternative technology that has lager potential energy output compared to biohydrogen, bioethanol, and biodiesel production. From this practical standpoint, biogas production from various macroalgae has been started in laboratory study (Table 4). The average biomethane yields of brown algae (0.262±0.057 m^3/kg volatile solids (VS)) represent a higher value than that of red algae (0.244±0.128 m^3/kg VS) and green algae (0.227±0.077 m^3/kg VS). Also, the yields data of brown algae were higher value than the terrestrial biomass of sugar crops (0.189±0.072 m^3/kg VS) and lignocellulosic biomass (0.172±0.113 m^3/kg VS) excepting organic wastes (0.332±0.076 m^3/kg VS) (Table 4).

Although the biomethane yields of brown algae are higher than those of other biomass resources, still fewer than 50% levels of theoretical value require further treatments which have applicable potential to increase the biomethane yields from brown algae. Indeed, dilution of the potential inhibitors (salt, polyphenols, and sulphated

Table 4. Comparison for the maximum biomethane yields data of biomass transition

Biomass	Feedstock[a]	Biomethane yield (m^3 CH_4/kg VS)	References
1st Generation	Sugar crop		
	Corn stover	0.107-0.241	[108,109]
	Sugarcane press mud	0.219	[110]
2nd Generation	Lignocellulosic biomass		
	Rice straw	0.281	[109]
	Wheat straw	0.245-0.258	[111]
	Cassava stalks	0.101	[112]
	Switchgrass	0.125	[113]
	Pine wood	0.020	[113]
	Organic wastes		
	Sewage sludge	0.273	[114]
	Animal waste	0.247-0.293	[90]
	Food waste	0.410-0.435	[115,116]
3rd Generation	Brown algae		
	Sargassum spp.	0.260-0.380	[46]
	Saccharina japonica	0.204-0.214	[117,118]
	Saccharina digitata	0.219	[119]
	Saccharina latissima	0.210-0.340	[120,121]
	Macrocystis pyrifera	0.281	[122]
	Undaria pinnatifida	0.283	[121]
	Saccorhiza polyschides	0.232	[121]
	Saccharina hyperborea	0.260	[123]
	Red algae		
	Gracilaria vermiculophylla	0.132-0.447	[120,124]
	Gracilaria verrucose	0.144	[121]
	Palmaria palmate	0.279	[121]
	Gracilaria tikvahiae	0.220	[125]
	Green algae		
	Ulva lactuca	0.152-0.271	[120,126]
	Chaetomorpha linum	0.166	[120]
	Codium tomentosum	0.158	[121]
	Ulva sp.	0.284-0.330	[118,125]

[a]No pretreatment

polysaccharides etc.) [85], nutrient balances between carbon and nitrogen (C/N ratio) [86], synergistic effects on microorganisms [87], and increasing the load of fermentable organics from feedstock [88] can be triggered via co-digestion, which is the simultaneous digestion of two or more feedstocks for enhancement of the methane production from macroalgae to achieve economic success (Table 5).

Thus far, only one large-scale plant of AD involving the Tokyo Gas Company working with the New Energy and Industrial Technology Development Organization of Japan has utilized cast brown algae (*Ulva* and *Saccharina* species) as feedstock and demonstrated the production of electricity and heat from biogas [26]. The tested plant was operated through mechanical pretreatment (5 m^3), anaerobic digestion (30 m^3), biogas upgrading & storage (30 m^3) and heat and power co-generation (Fig. 2). Retention time of VFA fermentation was 2 to 3 days at mesophilic condition (25-35 °C) before the methane digestion. The methane digester was operated 15 to 25 days retention time at thermophilic condition (55 °C). The yields of biogas were 17 and 22 m^3 CH_4 per one ton of *Ulva* and *Saccharina* sp., respectively. The biogas generated from both brown algae contained approximately 60% CH_4 and 40% CO_2 with several thousand ppms of H_2S. For desulfurization, the biogas was mixed with natural gas prior to supplying a gas combined heat and power (CHP) engine. The power output of the gas engine was held constant at 9.8 kW of electricity and 22.7 kW of heat. The electricity powered the AD plant, and heating capacity was also used internally to maintain the digester temperature. Because mixing fuel gases could contribute to lower concentration of CO_2 in biogas, attempts for adding natural city gas to biogas were made by regulating the heat level value of fuel gas. This case study indicates that brown algae are a potentially sustainable biogas resource to develop at large scale for the nearest future.

Table 5. The maximum biomethane yields data using co-digestion

Feedstock[a]	Biomethane yield (m^3 CH_4/kg VS)	References
Brown algae		
Saccharina spp.+*Ulva* spp.+milk	0.299	[73]
S. latissima+wheat straw	0.310	[86]
S. latistima+shrimp residues+sewage sludge	0.261	[123]
Red algae		
Gracilaria vermiculophylla+glycerol	0.615	[124]
G. vermiculophylla+sewage sludge	0.609	[124]
G. vermiculophylla+sewage sludge+glycerol	0.634	[124]
G. vermiculophylla+mixed sludge	0.298	[20]
Green algae		
Ulva lactuca+animal manure	0.440	[124]
Ulva sp.+*Cladophora* sp.+*Chaetomorpha* sp.	0.350-0.480	[125]
Ulva sp.+mixed sludge	0.315	[20]
Ulva sp.+primary sludge	0.360	[20]

[a]No pretreatment

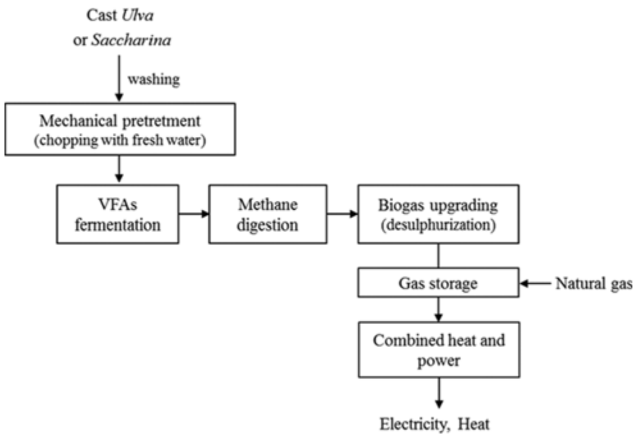

Fig. 2. Overall process scheme of Tokyo Gas pilot plant converting brown algae into electricity and heat energy [73].

IMPROVEMENT OF ANAEROBIC DIGESTION AND FUTURE POTENTIAL

To achieve the most promising for large scale application, the AD process from brown algae must be improved. The final goals for improving the AD process are both increasing the conversion efficiency and decreasing process operational and capital costs [89]. The core strategies for the improvement of AD process from biomass practically have included engineering of efficient operation and molecular biological monitoring with diagnosis [90]. The strategies can be also applied to brown algae; however, the presence of salt, polyphones and sulfated polysaccharides, which are specific characteristic of brown algae, requires to be carefully managed in order to prevent inhibition of the AD process and a lowering of biofuel yields [47,85].

To accomplish the successful large-scale utilization of brown algae,

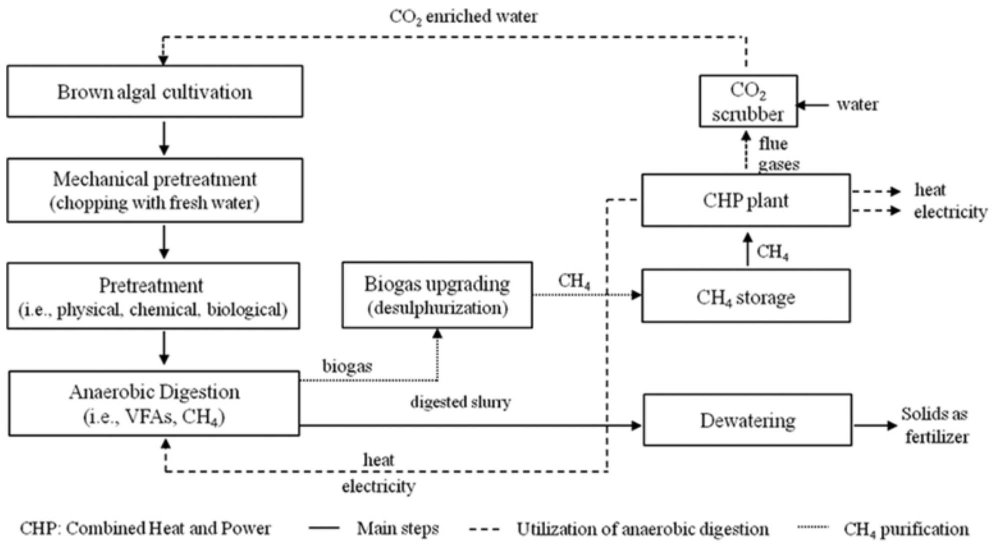

Fig. 3. Proposed future concept for integrated anaerobic digestion of brown algae into a carbon dioxide sequestration.

the integration of the AD into other biofuel conversion process and, as a result, improve their sustainability and energy balance [89], is necessary. The economic case assessment of integrated biofuels evaluated the feasibility of brown algae coupling biomethane of AD with bioethanol and hydrothermal liquefaction (HTL)-oil [46]. The estimated production cost of brown algae (*S. japonica*) including capital and operating costs was theoretically calculated ($112 per dry metric ton; [46]) from the cost analysis. Because the market price of edible brown algae ranges approximately $1,800 to $2,200 per dry ton [46], the economic feasibility of integrated biofuels platform can be developed.

Additionally, carbon dioxide emitted from power plants utilized for autotrophic algal assimilation (Fig. 3; [89]) can be a strategy for the near future. This strategy originates from biosequestration, which is the capture and storage of the atmospheric carbon dioxide by biological metabolic process, photosynthesis [91]. The potential attributed to wide distribution of the world coast, high biomass capability, fast CO_2 uptake and utilization, and, importantly, the ability to produce secondary products from the brown algae that are of high commercial value can strongly induce one to realize the economic success of biofuels platform in the future.

CONCLUSION

Early and more recent studies have shown the promising potential of brown algae as a biofuel feedstock from the AD process. Of course, though the utilization efficiency of alginate must be improved in the AD process, additional management of alginate such as pretreatment, removal inhibitors, and operational optimization can overcome the technical issues. To solve the fundamental economic challenge of marine brown algae as a sustainable biofuel feedstock, an integrated platform with various biofuels' production should be developed. Also, assimilation of carbon dioxide sequestration with the AD process from brown algae can contribute to realizing the renewable energy policy in the nearest future.

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