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Advances in the pretreatment of brown macroalgae for biogas production

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ABSTRACT

Brown macroalgae are an attractive, untapped resource and a favourable alternative for conventional fossil fuels, given their low lignin and high polysaccharide content. However, the restricted bioavailability of structurally complex carbohydrates for digestion, results in a low biomethane potential. This paper reviews the various pretreatment technologies explored to optimise saccharification prior to fermentation, categorised as: physical, biological, chemical, thermal and a combination of methods. A techno-economic assessment was conducted to evaluate the commercial viability of each process. Hydrothermal pretreatment proves the most promising technique for brown algae application, since it improves methane productivity, carries a net positive energy balance and generates a bio-fertilizer, while mitigating greenhouse gas emissions. Pilot scale research is necessary to evaluate the feasibility of full-scale implementation for brown algae bioconversion. A case study of the Cambi™ process concludes the paper as it exemplifies the successful utilisation of hydrothermal pretreatment for sewage sludge biogas production.

1. Introduction

Fossil fuels are the primary feedstock for global energy production, supplying 88% of the world's energy demand in 2008 [1]. However, the rising demand for this non-renewable resource, coupled with the volatility of oil prices, have rendered dependence on this commodity an unsustainable and unviable practice. Moreover, fossil fuel combustion negatively impacts environmental stability and promotes global warming through the emission of large volumes of the greenhouse gas (GHG), carbon-dioxide (CO_2) [2]. Between the 1970s and 2015, global CO_2 emissions rose by 3-fold from 11.75 to 35.72 gigatonnes (Gt), in direct proportion to fossil fuel consumption. Given the present CO_2 production rate of 630 million tonnes per annum, it has been postulated that by the year 2035, CO_2 emissions could reach 75 Gt [3]. It is therefore of paramount importance that alternative energy sources be found to abate fossil fuel utilisation, thereby supporting environmental conservation and sustainability [1,4].

Macroalgae or seaweeds have shown great promise as feedstock for bio-energy production because of their rich polysaccharide and negligible lignin content [5,6]. These large, multicellular marine organisms are abundant in nature and constitute approximately half of the world's biomass population [7,8]. Seaweeds fix atmospheric CO_2 for photosynthesis and propagate rapidly, due to a 4-fold greater photosynthetic efficiency than terrestrial biomass [9]. In 2000, 11.4 million wet tonnes of seaweed were harvested globally [10]. One decade later, the population of this marine biomass increased by nearly 200% to 19 million wet tonnes [11]. The accelerated growth rate of algae in recent years has been attributed to eutrophication and anthropogenic changes to environmental and oceanic conditions, as effected by elevated global atmospheric CO_2 levels [12].

Algae cultivation can occur independently of arable land, a freshwater supply and fertilizer application. These properties increase the appeal of utilising this natural resource for bio-energy production, since they offer little to no competition for the land space that would otherwise be occupied by traditional edible and energy crops [6,13].

While there is great uncertainty surrounding the number of macroalgal species in existence, approximately 10,000 to 12,500 species have been taxonomically classified [10,14]. Macroalgae can be subdivided into three groups based on algal pigmentation and thallus colour: red, green and brown algae (Fig. 1) [9,15].

Red algae (Rhodophyceae) are the most abundant type of macroalgae with approximately 6000 named species. Situated in the littoral and neritic zones of the ocean, these seaweeds acquire their characteristic red colour from the photosynthetic pigments phycoerythrin and phycocyanin. Chlorophyll A is also present within the cell structure and acts as an adaptation that facilitates maximum blue light absorption for photosynthetic growth, in waters ranging in depth from 40 to 250 m. Green algae (Chlorophyta) are a small group of 4500 species, present predominantly in freshwater habitats. These seaweeds contain chlorophyll A and B in a ratio equal to land plants and sit in the shallow

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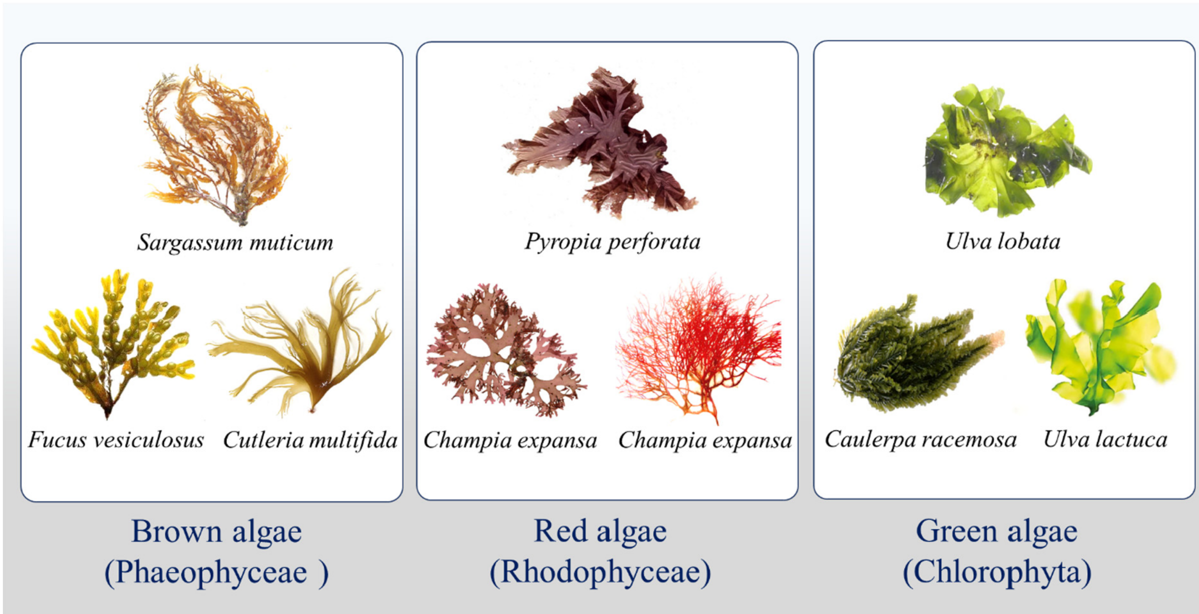

Fig. 1. Examples of different types of macroalgae.

region of the ocean for maximum light absorption.

Brown algae (Phaeophyceae) are the largest and most complex algal organisms, with approximately 2000 species in existence [9,12]. These seaweeds which grow in coastal waters of 30–50 m [16], acquire their characteristic dark-brown colour from elevated levels of the yellow-brown pigment fucoxanthin within their cell structure [17]. Brown macroalgae also possess a unique mechanism that promotes higher photon absorption during photosynthesis than in red and green algal species. Consequently, a larger number of brown seaweeds are present in marine environments [16].

One such brown macroalgal genus abundant in the world's ocean is *Sargassum*. This seaweed emanates in the Gulf of Mexico annually, then migrates along oceanic currents into the Sargasso Sea where it accumulates [18,19]. Satellite imaging has also revealed growth of this marine biomass in the North Equatorial Recirculation Region, a nutrient-dense zone situated between Brazil and the Equator [20]. In open water, pelagic Sargassum is the habitat to over 200 marine organisms [21]. However, within the last decade, the neritic waters and shorelines of the Caribbean, West Africa and Gulf of Mexico have experienced a deluge of drifting *Sargassum* blooms which threaten the survival of the Tourism and Fisheries sectors. Beach-cast *Sargassum* is unsightly and restricts ocean access by locals and visitors alike. Moreover, the anaerobic decomposition of shored *Sargassum* produces the pungent and toxic gas, hydrogen sulphide, which carries a noticeable and characteristic “rotten egg smell” [21,22]. This offensive odour was identified as the primary cause of reduced tourist arrivals to the Caribbean region in 2015 [23,24]. *Sargassum* influx is also responsible for mass fish kills across Belize and Mexico [25], and the death of dozens of endangered sea turtles in Barbados [26].

Brown macroalgae possess high levels of carbohydrates and proteins but exhibit a low lipid content [5]. This rich nutritional composition has contributed to their human consumption, inclusion into animal feed products and application as agricultural fertilisers [12,13]. Moreover, researchers have identified and extracted multiple bioactive compounds with potential in biosorption, pharmaceuticals and therapeutics [27,28]. Biofuel production from brown algae using anaerobic digestion (AD) technology has also been explored, as these seaweeds possess significantly less recalcitrant lignin than terrestrial crops [29,30]. Hitherto, the low specific methane yield (SMY) of brown algae makes it an unattractive feedstock for commercial biogas production downstream [16].

To enhance biomass solubilisation and the release of fermentable sugars for microbial digestion, pretreatment technologies have been investigated [5]. While these processes reveal great lab-scale potential, on-going research is necessary to determine their viability in the upsurging macroalgae-based biorefinery concept. This review paper details the progress made in brown macroalgae pretreatment and provides a comprehensive techno-economic assessment of each technique, based on the following industry process drivers: capital investment, net energy balance, process efficiency (PE) and environmental impact factor (EIF). From the methods studied, hydrothermal pretreatment using thermal hydrolysis is most advantageous for brown algae application and should be fully explored to evaluate scalability. Thermal hydrolysis is successfully exploited world-wide in several wastewater treatment facilities to improve the bioconversion of sewage sludge. The final section of this paper presents a case study on Cambi™, the world's leading thermal hydrolysis process (THP) and highlights the benefits derived from its implementation at Blue Plains in Washington DC.

2. Composition of brown macroalgae

Brown algae contain 70–90% moisture [9] and 10–15% ash [31]. When water is removed from these seaweeds, polysaccharides represent 40–60% [17,29], proteins 8–23% and lipids 0.3–6% of the dry weight (dw) content [21,32]. Microbial degradation of the proteins in this biomass is inhibited by cellular localisation [16], while the low lipid content has little impact on biofuel production [5,16]. Consequently, the biomethane potential (BMP) of brown macroalgae is dependent on the breakdown of carbohydrates [33]. The four sugars most abundant in brown algae are alginate, laminarin, mannitol and fucoidan [12]. However, the distribution of these sugars in seaweeds is disproportionate and varies with species, seasonality and the growth site conditions [16].

Alginate or alginic acid is the most abundant carbohydrate in the brown algae, representing approximately 40% dw of intracellular cell contents [33]. Present in the cell wall of algae where it supports mechanical strength [12], this linear sugar is composed of β-1,4-D-mannuronate and α-1,4-L-guluronate residues covalently bonded together [34]. Annually, the alginate levels in macroalgae peak during the summer months when light irradiance and saturation are at their highest, as an adaptation to prevent dehydrate. High alginate levels in summer also promote algal spawning by improving nitrate uptake and photosynthetic efficiency. While alginate metabolism is necessary for the effective bioconversion of macroalgae into biofuels, currently, industrial microbes are unable to assimilate this sugar. This challenge limits the energy potential of seaweeds for AD [12,13].

Laminarin is the major food storage polysaccharide which represents approximately one-third (35%) of the dw content of brown algae. This water-soluble polymer is composed of a linear β-1,3-D-glucose chain with interspersed branches of β-1,6-D-glucose. Structurally, laminarin contains weak glycosidic bonds which are easily broken during hydrolysis. This characteristic optimises the release of monomeric glucose units for AD. Laminarin is a product of photosynthesis and is greatest in quantity during spring and summer. Brown macroalgae proliferating in shallow coastal waters and inundated with solar radiation will therefore exhibit higher laminarin content than those inhabiting deeper waters [35,36].

Mannitol, an alcohol polymer of the sugar mannose, constitutes 20–30% dw of brown algae. This polysaccharide is the primary product of photosynthesis and can be easily hydrolysed by the enzyme mannitol dehydrogenase into fructose for subsequent conversion to bioethanol [35,37]. Similar to laminarin, the mannitol content of macroalgae also reaches a peak level during their photosynthetic growth phase. High mannitol levels are undesirable for AD as most microorganisms are unable to strictly anaerobically metabolise this sugar. During fermentation, mannitol is oxidised to fructose and NADH. However, to regenerate NAD+ and convert NADH to NADPH, a supply of oxygen or transhydrogenase is necessary [38]. Procaryotes contain transhydrogenase and can metabolise mannitol anaerobically [35].

Fucoidan is a water-soluble sulphated polysaccharide in brown algae [39]. This heterogeneous sugar is approximately one-fifth of the dw content of brown seaweed and composed of the carbohydrate fucose and sulfate, a nutrient fundamental for algal growth [40]. In addition to these two components, fucoidan contains the monosaccharides mannose, galactose, xylose, uronic and glucuronic acid [12,16]. Unlike laminarin and mannitol, fucoidan is prevalent during the autumn season, varying in quantity across species from 6 to 22% dw [39,41]. Macroalgae with low fucoidan content are preferred for AD as some fucans are resistant to anaerobic cleavage and inhibit fermentation [42].

3. Anaerobic digestion of brown macroalgae

AD is a cost-effective waste-to-energy technology. This multistep biological process takes place in an environment of little to no oxygen and involves the microbial decomposition of organic feedstock into biogas and a digestate. AD occurs in four stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis [43]. Hydrolysis is the rate-limiting step of AD as during this phase, structurally complex components such as lignin and cellulose are cleaved into their monomeric units, recalcitrant particulates are generated and the cumulative methane (CH_4) yield determined [44,45].

Biogas is a renewable energy source composed primarily of CH_4 (55–65%) and CO_2 (35–45%). CO_2 diminishes the energy value of biogas and can be removed through scrubbing. This purification process yields biomethane, a sustainable, eco-friendly substitute to conventional natural gas for application in electricity production, cooking and heating [43,44]. Capturing AD-derived CH_4 for energy recovery reduces its negative EIF. CH_4 is a GHG with a half-life of approximately one decade and global warming potential 20-fold greater than CO_2. In addition to biogas, a complementary nutrient-dense digestate is generated with application in agriculture as a soil conditioner [45,46].

Brown macroalgae are good feedstock for CH_4 fermentation given their rich carbohydrate composition and low lignin content. The high moisture level of this biomass also facilitates mass transfer between the substrate and micro-organisms, accelerating microbial growth and bioconversion [30,47]. The BMP of brown algae ranges from 204 to 380 mL/g VS. While this energy output is superior to the CH_4 yields achieved from sugar crops (241 mL/g VS), rice straw (281 mL/g VS), lignocellulosic biomass (101–258 mL/g VS), animal waste and sewage sludge (247–293 mL/g VS), it represents < 50% of the theoretical CH_4 potential [16]. The low bioconversion of brown seaweeds is attributed to the presence of complex polysaccharides which are not easily fermented, a mass carbon-to-nitrogen ratio below 20:1 and high levels of sulfur, polyphenols and salinity [5,48].

To address the challenge of low CH_4 productivity, pretreatment methods have been explored. These technologies increase the bioavailability of organic matter for microbial hydrolysis, thereby shortening the hydraulic retention time (HRT) and improving biogas formation [43,49]. Pretreatment techniques including physical, thermal, chemical, biological and a combination of methods have been applied to brown algae with varying success.

4. Physical pretreatment methods

4.1. Mechanical pretreatment

Mechanical pretreatment is a popular technique which involves the use of blades, knives and hammers to chip, grind, mill and shred biomass into small particles prior to AD. This process increases the reaction surface to volume ratio and liberates complex sugars for enzyme saccharification, thereby optimising bio-energy production [50,51] as shown in Table 1.

Ball milling is the primary treatment method applied to brown algae [52]. When *P. canaliculata* was pretreated for 60 min in a modified Hollander beater made of an elliptic channel, with a bladed drum rotating at 580 rpm, CH_4 recovery was 74% higher than the untreated sample [53]. Beating *Laminariaceae* spp. for 10 min also increased the concentration of volatile solids (VS) accessible for microbial degradation. Fermentation of the pretreated slurry for 21 d generated a total solids (TS) biogas production rate of 685 mL/g TS or 53% more biogas than that achieved from the raw feedstock [50]. Conversely, maceration had a negative impact on the biomethanation of *S. latissima,* diminishing the energy gains by 2% relative to the control [54].

4.2. Microwave pretreatment

Growing attention has been given by researchers to microwave irradiation as a replacement to conventional heating. Microwave pretreatment involves the use of short electromagnetic waves of frequencies ranging 0.3 to 300 GHz to rapidly heat the water in biomass to a boiling state, thereby creating pressure within the cells which breaks hydrogen bonds [46,55]. This method increases the concentration of the intracellular contents available for fermentation and improves the SMY. Microwave pretreatment has a marginal effect on biomass solubilisation [56,57].

To the authors' knowledge, only a single study exists on microwave-assisted extraction for brown algae biogas production. In this work by Montingelli et al. [44], *Laminaria* sp. was exposed to conventional microwave irradiation at 50 Hz and 560 W for 30s. These reaction conditions accelerated cellular disintegration and the concentration of organic matter released for microbial digestion. However, the bioconversion of this solubilised fraction was limited due to the presence of recalcitrant insoluble fibrous components. After 25 d of AD, the normalised CH_4 yield was 244 NmL/g VS. Compared to the untreated sample, microwave pretreatment decreased CH_4 production by 26% (see Table 1).

4.3. Ultrasound pretreatment

Ultrasound pretreatment or sonication involves the steady-state supply of rapid compression and depression cycles of sonic waves to biomass. During this treatment process, cell wall air cavities or

Table 1
Physical pretreatment of brown algae for biogas production.

Technique	Feedstock	Pretreatment conditions	AD process	HRT (d)	Incubation temp. (°C)	Results	Change in energy potential (%)	Reference
Mechanical	*Laminariaceae* spp.	Beating; 580 rpm; 10 min	Batch	21	50	430 mL CH_4/g TS	+53	[50]
	P. canaliculata	Beating; 580 rpm; 60 min	Batch	21	37	340 mL CH_4/g VS	+74	[53]
	P. canaliculata	Beating; 580 rpm; 10 min	Batch	21	37	444 mL biogas/g TS	+179	[67]
	F. serratus					181 mL biogas/g TS	+183	
	F. vesiculosus					231 mL biogas/g TS	+220	
	L. digitata					157 mL biogas/g TS	+52	
	F. vesiculosus	Washed; chopped (5 mm)	Batch	25	37	134 mL CH_4/g VS	+95	[68]
		Unwashed; chopped (5 mm)				120 mL CH_4/g VS	+75	
	F. vesiculosus	Pressure chamber (1000 bar)	Batch	52	37	92 NmL CH_4/g VS	+37	[69]
	Laminaria sp.	Beating; 580 rpm; 10 min	Batch	38	25	335 NmL CH_4/g VS	+1	[44]
		Ball milling (1 mm); 18 h				241 NmL CH_4/g VS	−27	
		Ball milling (2 mm); 18 h				260 NmL CH_4/g VS	−21	
	S. latissima	Washed; maceration	Batch	34	53	333 mL CH_4/g VS	−2	[54]
Microwave	*Laminaria* sp.	50 Hz; 560 W; 30 s	Batch	38	25	244 NmL CH_4/g VS	−26	[44]

microbubbles are formed and subsequently collapse, rupturing the cell envelope [55,58]. This change in the substrate morphology improves microbial access to fermentable sugars and promotes their bioconversion to CH_4 [59,60]. The composition and quantity of the organic matter released for AD varies with the sonication energy applied [61]. Optimum algal cell wall lysis occurs at high energy intensities and low frequencies ($<$ 100 kHz) [62]. The exposure time also impacts the efficiency of the sonication process. Long reaction times are favoured as they maximize cell destruction and the soluble chemical oxygen demand (COD) [63].

Ultrasonication has been applied to brown algae to improve the extraction of constituents such as laminarin, fucoidan and phytochemicals [64,65]. To date, no study has explored the effect of this pretreatment method on brown macroalgae methanation. However, from the literature available, sonication is suitable for wet biomass as the contained water facilitates the transmission of sound waves between the liquid and solid interfaces [66].

5. Biological pretreatment

Biological pretreatment is the process of applying micro-organisms (fungi, bacteria and enzymes) to biomass to degrade lignin and hemicellulose. This treatment process can occur either aerobically or anaerobically and improves both hydrolysis and biomethanation [70]. White rot fungi extracted from decaying wood are the most prominent microbes used in biological pretreatment. This fungus produces the enzymes lignin peroxidase, manganese peroxidase and laccase, which effectively fractionate lignin into CO_2 and water [71,72].

Few studies exist on optimising brown algae biogas production using biological pretreatment (Table 2). The application of the Bm-2 strain white rot fungi, *Trametes hirsuta*, to Mexican Caribbean macroalgae consortia for 6 d improved the degradation of lignocellulosic fibres and promoted the formation of grooves along the surface of this biomass. These physical modifications to the feedstock accelerated algal bioavailability and gave rise to the formation of 20% more biomethane than the raw sample after 29 d of retention time. Alternatively, enzyme pretreatment diminished CH_4 productivity by 6% [73]. Vanegas et al. [74] confirmed the negative performance of enzymes at improving the biogas productivity of L. *digitata*. The pretreatment of this algae with cellulase and alginate lyase for 24 h reduced bioconversion by 1 and 2%, respectively when compared to the untreated sample. Similarly, the application of celluclast 1.5 L to this seaweed lowered saccharification and the release of reducing sugars, thus diminishing biogas formation by 317%.

6. Chemical pretreatment

Strong and weak chemical reagents have been applied to biomass to improve cell wall disintegration, COD solubilisation and CH_4 production [46]. In alkali pretreatment, biomass simultaneously undergoes solvation and saponification. These reactions cleave the lignin and cellulose components, thereby increasing the concentration of sugars accessible for microbial digestion downstream. Comparatively, acidic reagents are more effective than alkalis at accelerating hemicellulose depolymerisation and delignifying biomass. The use of chemical reagents produces toxic organic acids which contaminate downstream products and alter the reactor pH, subsequently, inhibiting methanogenesis and inducing digester failure. To improve microbial proliferation and AD efficiency, alkaline compounds are added to the pretreated slurry prior to fermentation to neutralise the acidic environment [45].

Literature on the chemical pretreatment of brown algae is sparse (Table 3). Vanegas et al. [74] reported the production of 237 mL/g VS of biogas when L. *digitata* was pretreated with 2.5% citric acid for 1 h. This biogas yield was 4% higher than that generated from the untreated sample. Augmentation of the concentration to 6% citric acid enhanced the recovery of reducing sugars. However, this condition also promoted

Table 2
Biological pretreatment of brown algae for biogas production.

Micro-organisms	Feedstock	Pretreatment conditions	AD process	HRT (d)	Incubation temp. (°C)	Results	Change in energy potential (%)	Reference
Bm-2 strain white rot fungi, *Trametes hirsuta*,	Mexican Caribbean macroalgae consortia	35 °C; 6 d	Batch	29	35	104 mL CH_4/g VS	+20	[73]
Enzymatic broth		40 °C; 24 h				86 mL CH_4/g VS	−6	
Cellulase	*L. digitata*	37 °C; 24 h	Batch	32	35	225 mL biogas/g VS	−1	[74]
Alginate lyase		37 °C; 24 h				232 mL biogas/g VS	−2	
Celluclast 1.5 L		40 °C; 24 h				72 mL biogas/g VS	−317	
1% enzyme mix of cellulase, hemicellulase, pectinase and protease	*F. vesiculosus*	50 °C; 5 h	Batch	52	37	49 NmL CH_4/g VS	−27	[69]

the formation of inhibitory compounds such as furfural and phenols which suppress microbial hydrolysis and biogas productivity. Consequently, at 6% citric acid, the biogas yield decreased by 330% to 69 mL/g VS.

7. Thermal pretreatment

In thermal pretreatment, temperatures ranging from 50 to 250 °C are applied directly to the surface of biomass via heat exchange to break the hydrogen bonds that maintain mechanical strength, effecting cell wall disintegration. This structural change to the substrate improves the enzymatic hydrolysis of organic matter and results in higher biogas yields [46,52]. Thermal pretreatment can be sub-divided into low temperature (< 110 °C) and high temperature (> 110 °C) reactions. High temperature reactions are favoured as they optimise biomass solubilisation and energy extraction. However, temperatures beyond 180 °C promote the formation of inhibitory compounds such as furfural, hydroxymethylfurfural and phenols which reduce the efficiency of bioconversion [63,75].

Autoclaving *Sargassum* sp. at 121 °C and 1 bar for 15 min increased the soluble VS content by 10-fold. The SMY obtained after pretreatment increased by 60% compared to the unpretreated algae [76].

Hydrothermal or pressurized hot water pretreatment is an alternative to conventional thermal processing. In this method, biomass is cooked in water or steam at temperatures and pressures ranging from 110 to 180 °C and 6–25 bar, respectively [77,78] without the addition of chemicals or enzymes [79]. Under these subcritical conditions, the hydrogen bonds in water are broken, consequently improving its solvation, biochemical and reactivity properties [80,81]. Hydrothermal processing increases polysaccharide solubilisation and CH_4 productivity but shortens the fermentation time [77,82].

In literature, hydrothermal pretreatment has been applied to brown algae with great success. *S. latissima* was exposed to steam explosion at 130 and 160 °C, for 10 min, respectively. Using a steam explosion facility designed by Cambi AS, the treatment process enhanced biomass disintegration and enzymatic hydrolysis. After a retention time of 119 d, biomethane recovery increased by 17–20% relative to the raw sample [6]. Hot water pretreatment of *Nizimuddinia zanardini* at 121 °C for 30 min accelerated organic matter solubilisation and enhanced the release of monomeric glucose units for AD. This treatment process was also advantageous, improving the quantity and purity of the CH_4 fraction generated by 22 and 2%, respectively, compared to untreated seaweeds [83].

Lower temperature water pretreatment has also been explored. However, reaction temperatures < 80 °C are ineffective and diminish the BMP [84]. In a study conducted by Barbot et al. [85], *F. vesiculosus* was pretreated with water heated to three different temperatures for 24 h. At the reaction temperatures of 20 and 50 °C, the authors reported decreases of 19 and 21% in the SMY, respectively. On the contrary, the application of hot water (80 °C) improved microbial digestion and yielded 51% more CH_4 than the raw algae. Table 4 summarises the effect of thermal pretreatment methods on the bioconversion of brown seaweeds.

8. Combined pretreatment methods

To improve biomass enzymatic hydrolysis and the corresponding BMP, multiple pretreatment combinations have been explored (see Table 5). While combined pretreatments are highly complex, they are more effective than the standard treatment procedures [46].

Thermo-chemical pretreatment is the primary combination studied. Pretreatment of *F. vesiculosus* with 0.2 M industry-grade HCl at 80 °C for 90 min improved enzymatic hydrolysis and promoted the recovery of 121 mL CH_4/g VS after 22 d of retention time. This CH_4 yield was 39% higher than that achieved from the untreated sample. Substituting HCl with less acidic flue gas condensate (FGC) exhibited a poorer

Table 3
Chemical pretreatment of brown algae for biogas production.

Technique	Feedstock	Medium	Pretreatment conditions	AD process	HRT (d)	Incubation temp. (°C)	Results (mL biogas/g VS)	Change in energy potential (%)	Reference
Acid	*L. digitata*	2.5% citric acid	120 °C; 1 h; 1 atm	Batch	32	35	237	+ 4	[74]
		1% lactic acid					161	− 42	
		6% lactic acid					101	− 226	
		6% oxalic acid					83	− 275	
		6% citric acid					69	− 330	

pretreatment performance, increasing biomethanation by 24%. Conversely, the application of acidic media of concentrations below 0.1 M have a negative effect on biodegradation and CH_4 productivity [84]. In a secondary study, the pretreatment of *F. vesiculosus* with 0.2 M HCl at 80 °C for 2 h generated 108 mL/g VS of CH_4. Augmenting the treatment time from 2 to 24 h marginally enhanced CH_4 recovery to 113 mL/g VS [85]. For optimum bioconversion of this biomass to be achieved, the correct balance of acidity and exposure temperature must be established [84].

Mechano-biological pretreatment increased the concentration of soluble COD released from *F. vesiculosus* by 3.5-fold relative to the untreated algae. In this work, the feedstock was pretreated mechanically in a TK Energi AS prototype machine pressurized to 1000 bar and subsequently incubated at 50 °C with a 1% mix of the four enzymes: cellulase, hemicellulase, pectinase and protease. After fermentation for 52 d, the volume of CH_4 extracted was 96% higher than the untreated biomass [69].

The effect of enzyme-acid pretreatment on reducing sugar and biogas production has been studied by Vanegas et al. [74]. In this work, the brown seaweed L. *digitata* was pretreated with various organic acids and enzymes. The authors observed a linear increase in biomass hydrolysis and reducing sugar release with the concentration of acid used. However, at high acid concentrations, inhibitory compounds such as furfural and phenols were formed. These compounds altered the pH of the digester and inhibit microbe proliferation, subsequently reducing biogas production. Optimum biogas recovery of 243 mL/g VS was achieved after combined pretreatment with cellulase and 2.5% citric acid.

In a recent study, *L. japonica* was exposed to combined microwave-acid pretreatment. At all the treatment acid conditions studied, biomass disintegration and saccharification improved. However, the degree of COD solubilisation increased in direct proportion to the acid concentration. Maximum hydrogen production of 28 mL/g TS was achieved with microwave pretreatment (2450 MHz, 140 °C) and 1% sulfuric acid for 15 min [86]. This combined pretreatment process exhibits great promise and should be explored further as a potential pretreatment method for improving brown algae CH_4 production.

9. Techno-economic assessment and energy balance

Biomass pretreatment methods have proven to be effective at improving cell wall disintegration, COD solubilisation and CH_4 production. However, the transition of these technologies from laboratory scale study to industry is hindered by several technical, economic and environmental challenges [16,87].

Mechanical pretreatment methods are energy-intensive processes with low EIF. While these technologies function independently of chemical and enzyme additives, the purchase price of specialized equipment and high electricity consumption rates inflate the capital and operational expenditures [45]. Microwave pretreatment is advantageous as electrical power is quickly converted to heat and uniformly distributed to the feedstock. However, this technology demands large energy input given the high irradiation power and extended exposure time necessary [46]. Similarly, ultrasonication requires a high specific energy input of 205–900 kJ/L and lengthy treatment time [88]. Physical pretreatment methods are energy inefficient and carry net negative energy balances. Collectively, these variables reduce the economic feasibility of commercialisation [46,69].

Physical pretreatments are most effective with feedstock of > 14% VS and > 6% TS [46]. Brown algae exhibit low VS content due to high moisture levels. Water also increases the shear strength of this feedstock, thereby reducing cell wall disruption and polysaccharide solubilisation [43]. To improve biomass degradation and VS content, a dewatering phase should be incorporated prior to pretreatment. While the inclusion of this step would achieve a positive energy balance, the additional energy demanded would incur operational and maintenance (O&M) costs [89].

By comparison, biological pretreatment requires a lower capital investment and energy input than physical and thermo-chemical pretreatment methods [90,91]. This process is safe and eco-friendly, generating no inhibitors and emitting no harmful compounds into the atmosphere [70,92]. The deployment of this technology is primarily affected by the high cost of enzymes [46]. The enzymes used for hydrolysis can either be cultured on-site or sourced externally. On-site enzyme production is financially advantageous as it eliminates the need for stabilizers to extend the shelf life of enzymes, reduces transportation costs, nullifies the impact of fluctuating enzyme market prices and supports the development of substrate specific microbial consortia

Table 4
Thermal pretreatment of brown algae for biogas production.

Technique	Feedstock	Pretreatment conditions	AD process	HRT (d)	Incubation temp. (°C)	Results (mL CH_4/g VS)	Change in energy potential (%)	Reference
Autoclaving	*Sargassum* sp.	121 °C; 1 bar; 30 min	Batch	42	37	541	+ 60	[76]
Hydrothermal	*F. vesiculosus*	20 °C; 24 h	Batch	20	37	38	− 19	[85]
		50 °C; 24 h				37	− 21	
		80 °C; 24 h				71	+ 51	
	F. vesiculosus	80 °C; 2 h	Batch	22	37	80	− 9	[84]
	Nizimuddinia zanardini	121 °C; 30 min	Batch	40	37	143	+ 22	[83]
Steam explosion	*S. latissima*	130 °C; 10 min	Batch	119	37	268	+ 20	[6]
		160 °C; 10 min				260	+ 17	

Table 5
Combined pretreatments of brown algae for biogas production.

Technique	Feedstock	Reagent	Pretreatment conditions	AD process	HRT (d)	Incubation temp. (°C)	Results	Change in energy potential (%)	Reference
Thermal + chemical	*F. vesiculosus*	0.05 M HCl	80 °C; 2 h	Batch	22	37	66 mL CH_4/g VS	−32	[84]
		0.1 M HCl	80 °C; 2 h				95 mL CH_4/g VS	+9	
		0.2 M HCl	80 °C; 30 min				90 mL CH_4/g VS	+4	
			80 °C; 60 min				94 mL CH_4/g VS	+8	
			80 °C; 90 min				121 mL CH_4/g VS	+39	
			80 °C; 2 h				98 mL CH_4/g VS	+13	
			100 °C; 2 h				103 mL CH_4/g VS	+24	
		HCl pH 1.2	80 °C; 2 h				103 mL CH_4/g VS	+18	
		FGC pH 1.2	80 °C; 2 h				108 mL CH_4/g VS	+24	
	F. vesiculosus	0.2 M HCl	20 °C; 24 h	Batch	20	37	52 mL CH_4/g VS	+11	[85]
			50 °C; 24 h				86 mL CH_4/g VS	+83	
			80 °C; 2 h				108 mL CH_4/g VS	+130	
			80 °C; 4 h				107 mL CH_4/g VS	+128	
			80 °C; 6 h				101 mL CH_4/g VS	+115	
			80 °C; 12 h				116 mL CH_4/g VS	+147	
			80 °C; 24 h				113 mL CH_4/g VS	+140	
Thermal + chemical	*F. vesiculosus*	FGC	20 °C; 24 h	Batch	20	37	37 mL CH_4/g VS	−21	[85]
			50 °C; 24 h				41 mL CH_4/g VS	−13	
			80 °C; 24 h				65 mL CH_4/g VS	+38	
Mechanical + biological	*F. vesiculosus*	Pressure chamber, 1% enzyme mix of cellulase, hemicellulase, pectinase and protease	1000 bar; 50 °C	Batch	52	37	131 NmL CH_4/g VS	+96	[69]
Biological + chemical	*L. digitata*	Cellulase, 2.5% citric acid	120 °C; 1 h	Batch	32	35	243 mL biogas/g VS	+6	[74]
		Cellulase, 1% lactic acid					219 mL biogas/g VS	−4	
		Cellulase, 1% oxalic acid					176 mL biogas/g VS	−30	
		Cellulase, 6% lactic acid					99 mL biogas/g VS	−230	
		Cellulase, 6% oxalic acid					76 mL biogas/g VS	−300	

[91,93]. Additional drawbacks to the industrialization of this method include a slow hydrolytic rate, large reactor device and negligible enhancements on biomass solubilisation and biogas productivity. While brown algae are suitable feedstock for biological pretreatment, the stated challenges reduce the economic feasibility of full-scale implementation [46,92].

Chemical pretreatment is the costliest method studied. While the energy consumed during operation is low, great investment is required to purchase the reactor and chemical additives [93]. Chemicals reagents are expensive, varying in price by supplier and with market value. These compounds are also corrosive and promote digester erosion. Consequently, high-grade corrosion resistant materials are used in reactor construction [46,94]. At high chemical concentrations, biomass solubilisation is optimised. However, these harsh reaction conditions have a minor effect on biogas production and accelerate digester attrition, thereby compounding O&M costs [45,95]. Acid/alkaline pretreatment also produces a slurry infused with AD inhibitory organic acids [93]. Neutralisation of these acidic compounds prior to fermentation incurs additional operation charges [79]. Chemical pretreatment is too harsh for macroalgae application and should be limited to lignocellulose-dense biomass [45,52].

Thermal pretreatment is a simple process with an implementation cost that varies according to the reaction temperature and the exposure time [94]. This technology is advantageous, demanding lower energy input than physical pretreatment methods and eliminating the need for expensive chemicals and enzymes [90,95]. At reaction temperatures > 110 °C, thermal hydrolysis can be corrosive. To reduce the effect, high-grade corrosion resistant materials are used in reactor construction, increasing the capital and maintenance costs [91]. The energy balance of thermal pretreatment varies with the feedstock TS content. When this process is applied to macroalgae, the net energy balance is negative due to its high water content which restricts the transfer of heat from the reactor to the substrate [44,75]. As with physical pretreatments, dewatering prior to pretreatment is imperative to improve the bioconversion efficiency and achieve a net positive energy balance [46].

Hydrothermal pretreatment consumes more energy than conventional thermal pretreatment due to the reaction configuration of elevated temperature and pressure, coupled with the steady state supply of water into the reactor device [87,93]. However, this process is thermodynamically viable as the energy generated from the biogas produced is superior to the energy consumed during operation [45,79]. The technology also sanitizes, dewaters and reduces the viscosity of biomass, thereby improving the nutritional quality of the digestate generated during AD [46]. Hydrothermal pretreatment can successfully accommodate feedstock of high water content and is most suitable for commercial brown algae biogas production.

Several combined pretreatment methods have been explored but the high cost of energy, chemicals reagents and enzymes is the major factor hindering their full-scale application [46]. Thermo-chemical pretreatment is the only combination currently exploited for sewage sludge wastewater treatment [45]. While this technology effectively enhances organic matter solubilisation and anaerobic digestibility, the operating conditions employed are not suitable for brown macroalgae application. Moreover, the process carries a negative energy balance and is detrimental to environment stability [84]. Table 6 summaries the techno-economic study.

In summary, the economic feasibility of full-scale pretreatment implementation relies primarily on the process energy balance. While most of the methods explored enhance anaerobic biodegradability and biogas productivity, they demand high energy inputs and exhibit net negative energy balances when applied to algal biomass. To date, hydrothermal pretreatment is the single energy-efficient technology studied. However, prior to the industrial establishment of this technology for resource recovery purposes, consideration must also be given to variables such as the technology readiness level and net present value, which are critical for the development, sustainability and economic performance of bio-based production processes [96,97]. Pilot scale research should therefore be conducted to evaluate the commercial viability of introducing this technology, for commercial brown seaweed biogas production. Several hydrothermal pretreatment technologies such as Cambi™, Biothelys™ and Exelys™ are globally available in wastewater treatment plants (WWTPs) to improve the bioconversion of sewage sludge [98]. The following section presents a case study on Cambi, the world's leading THP.

9.1. Case study: the Cambi™ process

9.1.1. Technology

Cambi AS is a Norwegian-based company that develops and implements green, reliable and cost-effective technologies for biowaste treatment and disposal. Established in 1989 by the forest owners' association Glommen Skogeierforening, this company is presently the global leader in the deployment of a patented eco-friendly and sustainable THP which treats and improves the conversion of sewage sludge and organic waste into bio-energy [99,100]. Cambi THP occurs in a reactor and involves the direct injection of saturated steam into dewatered biomass at 16–18% dry solids (DS), for 20–30 min at 165 °C and 5–6 bar. Thereafter, the system is suddenly depressurised to 4 bar, triggering a “steam explosion” [99]. This pretreatment process increases the breakdown of the cellular structure and fibrous components in sewage sludge, thereby accelerating microbe accessibility to biodegradable contents for fermentation. The incorporation of Cambi THP prior to fermentation achieves < 60% cell disintegration and yields a biogas fraction approximately 50% greater than that recovered from conventional AD [100,101].

The biogas derived from AD is cleaned and transferred to a combined heat and power facility for the co-generation of electricity and steam. The electricity produced is externally supplied for consumption while the steam is recycled into the treatment facility to power the thermal hydrolysis of influent sludge. Utilisation of steam in THP is advantageous as it mitigates the demand for fossil fuels, the carbon footprint and the total operation cost. Cambi THP also improves dewatering and lowers biosolid production by 50–70%, thus supporting public health and environmental sustainability, by reducing landfill disposal and the corresponding GHG emissions. The biosolids formed are low odour, nutrient-rich and pathogen-free with application in agriculture to promote crop productivity and amend soil health [99,100]. Collectively, these properties contribute to the global appeal of Cambi THP implementation [102]. The schematic diagram below (Fig. 2) details the Cambi™ THP.

In 1995, the first full-scale Cambi THP facility was commissioned in Hias, Norway. However, by 2012, the number of WWTPs equipped with Cambi units had risen to 26 world-wide. Collectively, annually, these systems have the treatment capacity of 530,000 t of DS of sewage sludge and can co-generate 1900 GWh of thermal energy and 760 GWh of electrical power, for supply to 26 million residents. At optimum PE and capacity, Cambi plants could accommodate 768,000 t DS of sewage sludge per annum. The incorporation of this green technology into AD plants as a pretreatment step is environmentally advantageous, mitigating the formation of 760,000 t of fossil fuel- derived CO_2 emissions and reducing total CH_4 emissions by 2.5 million tonnes of CO_2 equivalent [103]. Effective December 2018, Cambi THP provides electricity to approximately 75 million households, through the installation of 65 biogas plants in 22 countries, across 5 continents. Cambi THP plant sizes range from 10 to 450 t DS/d and carry a combined treatment capacity of 7050 t DS/d. Noteworthy, the present installed capacity of Cambi THP adopted in the United Kingdom can treat 56% of the country's sewage sludge waste stream [102].

9.1.2. Blue Plains advanced wastewater treatment facility

Blue Plains located in Washington DC, USA, is the world's largest

Table 6
Comparison of brown algae pretreatment technologies.

Technology	Physical			Biological	Chemical		Thermal			Combined
Parameters	Mechanical	Microwave	Ultrasound		Acid	Base	(< 110 °C)	(> 110 °C)	Hydrothermal	Thermochemical
Capital investment	+ + +	+ + +	+ + +	+ +	+ + +	+ + +	+	+ + +	+ + +	+ + +
O&M costs	+ +	+ +	+ +	+ +	+ +/+ + +	+ +	+	+ +	+/+ +	+ + +
Energy demand	+ + +	+ + +	+ + +	+	+	+	+	+ +	+ + +	+ + +
Algal solubilisation	NA	+	+	+	+ + +	+ +	+	+ +	+ + +	+ + +
PE	+ +	+	NS	−/+	−	NS	−	+/+ +	+ +/+ + +	+ +/+ + +
EIF	+	+	+	+	+ + +	+ +	+ + +	+ +	+	+ +/+ + +
Odour generation	+	+	+	+ + +	+ + +	+ + +	+ +	+ +	+	+ + +
Pathogen removal	+	+	+	+ + +	+	+	+ +	+ + +	+ + +	+/+ +
Application to brown macroalgae	+ + +	+	NS	+	+	NS	+	+	+ +	+ +

NA: Not applicable; NS: Not studied; −: negative; +: low; + +: moderate; + + +: high.

advanced WWTP and the first facility in North America to adopt the Cambi THP into its operation. Managed and operated by the District of Columbia Water and Sewer Authority (DC Water) and occupying approximately 160 acres, this plant was deployed in 1938, as the primary sewage treatment facility servicing the states of Washington DC, Maryland and Virginia. The effluent emanating from DC Water Blue Plains is discharged into the adjacent Potomac River [104].

In 1959, the treatment capacity of Blue Plains was 240 million gallons of sewage per day. Structural modifications were subsequently made to the facility in 1983, augmenting the digestion capacity to 300 million gallons in response to the growing energy demand and waste production rate. Most recently, in 2014, the existing WWTP was retrofitted with a US $407 million Cambi™ AS pretreatment system. The new facility hosts four large anaerobic digesters, each of volume 3.8 million gallons and combined capacity 58,100 m^3. Daily this plant treats 370–390 million gallons of water at a rate of 15 m^3/s. At peak operation capacity and during periods of heavy rainfall or large storms, these units can receive in excess of 1 billion gallons per day [99,100].

9.1.3. Economic and environmental viability

Cambi THP systems give a positive energy balance and are 35% less costly than conventional AD digesters, accruing capital savings of US $200 million due to higher net biogas production. At the DC Water facility, the use of recycled steam to power the operation mitigates fossil fuel dependency by 33% and energy costs by US $10 million annually [98,100]. In 2016, this plant supplied 13 MW of electricity to approximately 2.2 million customers at a lower rate than conventional petroleum-based energy companies. By 2020, the projected power output from this plant is predicted to be 20 MW [98,105]. Thermal hydrolysis produces a small volume of class A biosolids (> 50%) downstream, mitigating expenditure on lime stabilizers, hauling and landfill disposal by US $10 million annually [99]. The biosolids generated are packaged and consumed both locally and internationally as a biofertiliser, thus gaining foreign exchange. The incorporation of Cambi THP into Blue Plains also improves air quality, eliminating GHG emissions by 40% or the equivalent of 47,000–73,000 t of CO_2 annually [98,100].

10. Conclusions and recommendations

Brown macroalgae are viable feedstock for bio-energy production given their unique physicochemical properties. However, the

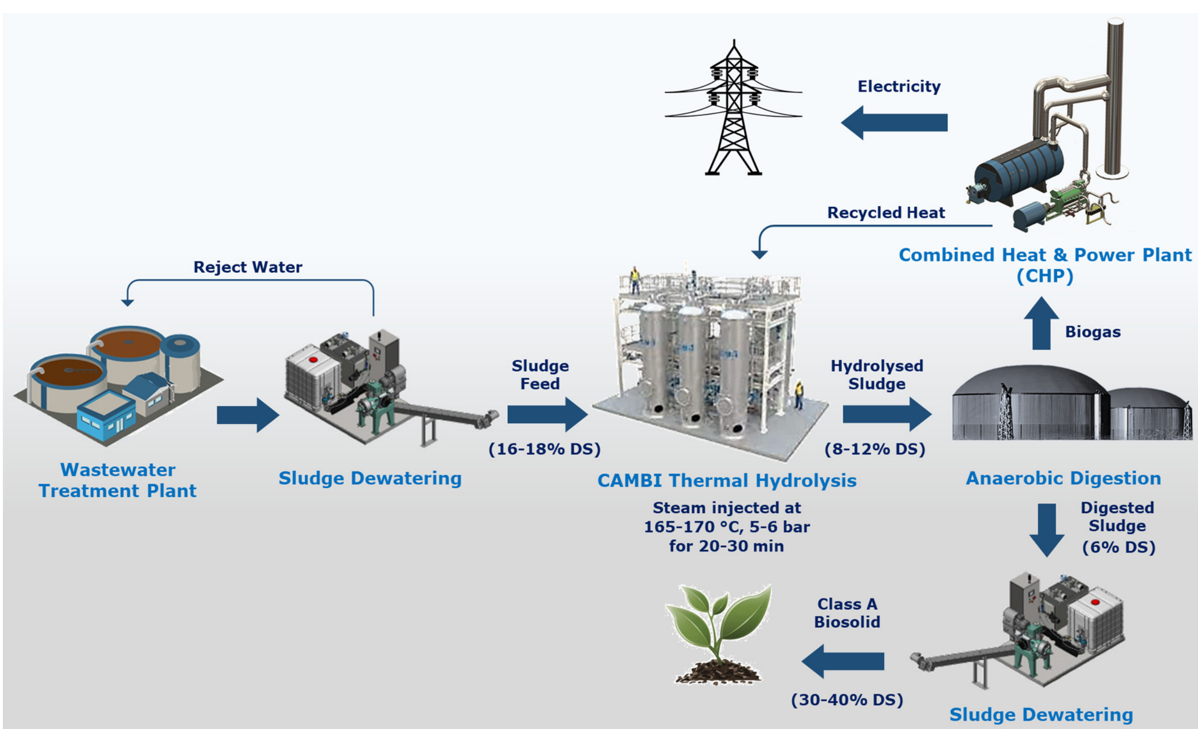

Fig. 2. Cambi™ THP configuration.

bioconversion of these seaweeds is limited by the inaccessibility of complex sugars for microbial degradation. Pretreatment technologies improve the efficiency of saccharification and fermentation but require high capital investment and significant energy inputs. From the techno-economic assessment conducted, hydrothermal pretreatment is the most feasible and attractive technology for this marine biomass. Hitherto, hydrothermal pretreatment has been exploited in WWTPs to optimise biogas production from sewage sludge. Future research efforts should focus on the pilot-scale studies to validate the utilisation of this technology in industry and investigate its scalability for the commercial valorization of brown algae into biogas.

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References

[1] L. Brennan, P. Owende, Biofuels from microalgae - a review of technologies for production, processing, and extractions of biofuels and co-products, Renew. Sust. Energ. Rev. 14 (2010) 557–577, https://doi.org/10.1016/j.rser.2009.10.009.
[2] S.H. Mohr, J. Wang, G. Ellem, J. Ward, D. Giurco, Projection of world fossil fuels by country, Fuel 141 (2015) 120–135, https://doi.org/10.1016/j.fuel.2014.10.030.
[3] N. Abas, A. Kalair, N. Khan, Review of fossil fuels and future energy technologies, Futures 69 (2015) 31–49, https://doi.org/10.1016/j.futures.2015.03.003.
[4] M. Meinshausen, N. Meinshausen, W. Hare, S.C.B. Raper, K. Frieler, R. Knutti, et al., Greenhouse-gas emission targets for limiting global warming to 2°C, Nature 458 (2009) 1158–1162, https://doi.org/10.1038/nature08017.
[5] M.E. Montingelli, S. Tedesco, A.G. Olabi, Biogas production from algal biomass: a review, Renew. Sust. Energ. Rev. 43 (2015) 961–972, https://doi.org/10.1016/j.rser.2014.11.052.
[6] V. Vivekanand, V.G.H. Eijsink, S.J. Horn, Biogas production from the brown seaweed Saccharina latissima: thermal pretreatment and codigestion with wheat straw, J. Appl. Phycol. 24 (2012) 1295–1301, https://doi.org/10.1007/s10811-011-9779-8.
[7] A.S. Carlsson, J.B. van Beilen, R. Möller, D. Clayton, Micro-and macro-algae: utility for industrial applications: outputs from the EPOBIO project, http://www.etipbioenergy.eu/images/epobio_aquatic_report.pdf, 2007 (accessed 27 December 2018).
[8] P. Chen, M. Min, Y. Chen, L. Wang, Y. Li, Q. Chen, et al., Review of biological and engineering aspects of algae to fuels approach, Int. J. Agr. Biol. Eng. 2 (2010) 1–30, https://doi.org/10.3965/j.issn.1934-6344.2009.04.001-030.
[9] K.A. Jung, S.R. Lim, Y. Kim, J.M. Park, Potentials of macroalgae as feedstocks for biorefinery, Bioresour. Technol. 135 (2013) 182–190, https://doi.org/10.1016/j.biortech.2012.10.025.
[10] J.D. Murphy, B. Drosg, E. Allen, J. Jerney, A. XiA, C. Herrmann, A perspective on algal biogas, in: D. Baxter (Ed.), IEA Bioenergy, 2015, pp. 1–38. https://www.ieabioenergy.com/publications/a-perspective-on-algal-biogas/.
[11] FAO, The state of world fisheries and aquaculture, Contributing to Food Security and Nutrition for all, Rome, 2016, pp. 200. http://www.fao.org/3/a-i 5555e.pdf.
[12] N. Wei, J. Quarterman, Y.-S. Jin, Marine macroalgae: an untapped resource for producing fuels and chemicals, Trends Biotechnol. 31 (2013) 70–77, https://doi.org/10.1016/j.tibtech.2012.10.009.
[13] A.J. Wargacki, E. Leonard, M.N. Win, D.D. Regitsky, C.N.S. Santos, P.B. Kim, et al., An engineered microbial platform for direct biofuel production from brown macroalgae, Science 335 (2012) 308–313, https://doi.org/10.1126/science.1214547.
[14] M.D. Guiry, How many species of algae are there? J. Phycol. 48 (2012) 1057–1063, https://doi.org/10.1111/j.1529-8817.2012.01222.x.
[15] G. Jard, H. Marfaing, H. Carrère, J.P. Delgenes, J.P. Steyer, C. Dumas, French Brittany macroalgae screening: composition and methane potential for potential alternative sources of energy and products, Bioresour. Technol. 144 (2013) 492–498, https://doi.org/10.1016/j.biortech.2013.06.114.
[16] M. Song, H.D. Pham, J. Seon, H.C. Woo, Marine brown algae: a conundrum answer for sustainable biofuels production, Renew. Sust. Energ. Rev. 50 (2015) 782–792, https://doi.org/10.1016/j.rser.2015.05.021.
[17] K. Miyashita, N. Mikami, M. Hosokawa, Chemical and nutritional characteristics of brown seaweed lipids: a review, J. Funct. Foods 5 (2013) 1507–1517, https://doi.org/10.1016/j.jff.2013.09.019.
[18] J. Gower, E. Young, S. King, Satellite images suggest a new Sargassum source region in 2011, Remote Sens. Lett. 4 (2013) 764–773, https://doi.org/10.1080/2150704X.2013.796433.
[19] J.F.R. Gower, S.A. King, Distribution of floating Sargassum in the Gulf of Mexico and the Atlantic Ocean mapped using MERIS, Int. J. Remote Sens. 32 (2011) 1917–1929, https://doi.org/10.1080/01431161003639660.
[20] S. Djakouré, M. Araujo, A. Hounsou-Gbo, C. Noriega, B. Bourlès, On the potential causes of the recent pelagic Sargassum blooms events in the tropical North Atlantic Ocean, Biogeosci. Discuss. doi:https://doi.org/10.5194/bg-2017-346 (in review 2017).
[21] J. Milledge, P. Harvey, Golden tides: problem or golden opportunity? The valorisation of Sargassum from beach inundations, J. Mar. Sci. Eng. 4 (2016) 60, https://doi.org/10.3390/jmse4030060.
[22] V. Smetacek, A. Zingone, Green and golden seaweed tides on the rise, Nature 504 (2013) 84–88, https://doi.org/10.1038/nature12860.
[23] C. Hinds, H. Oxenford, J. Cumberbatch, F. Fardin, E. Doyle, A. Cashman, Golden tides: management best practices for influxes of Sargassum in the Caribbean with a focus on clean-up, https://www.cavehill.uwi.edu/cermes/getdoc/123bf91c-1565-414d-8e21-e59fb6f7ca2d/cermes_sargassum_management_brief_2016_08_24.aspx, 2016 (accessed 6 June 2018).
[24] D. Bolton, Stinking Seaweed on Caribbean Beaches Causes Tourists to Cancel Holidays, https://www.independent.co.uk/news/world/americas/stinking-sargassum-seaweed-on-caribbean-beaches-causes-tourists-to-cancel-holidays-10448743.html, 2015 (accessed 3 June 2018).
[25] The San Pedro Sun. Belizean Beaches Overwhelmed by Tons of Sargassum, https://www.sanpedrosun.com/environment/2015/03/23/belizean-beaches-overwhelmed-by-tons-of-sargassum/, 2015 (accessed 4 June 2018).
[26] H-L. Evanson, Turtle Victims, http://www.nationnews.com/nationnews/news/69374/turtle-victims, 2015 (accessed 13 June 2018).
[27] R. Dhankhar, A. Hooda, Fungal biosorption—an alternative to meet the challenges of heavy metal pollution in aqueous solutons, Environ. Technol. 32 (2011) 467–491, https://doi.org/10.1080/09593330.2011.572922.
[28] E.M. Balboa, E. Conde, A. Moure, E. Falqué, H. Domínguez, In vitro antioxidant properties of crude extracts and compounds from brown algae, Food Chem. 138 (2013) 1764–1785, https://doi.org/10.1016/j.foodchem.2012.11.026.
[29] A.B. Ross, J.M. Jones, M.L. Kubacki, T. Bridgeman, Classification of macroalgae as fuel and its thermochemical behaviour, Bioresour. Technol. 99 (2008) 6494–6504, https://doi.org/10.1016/j.biortech.2007.11.036.
[30] R. Paul, L. Melville, M. Sulu, Anaerobic digestion of micro and macro algae, pretreatment and co-digestion - biomass - a review for a better practice, Int. J. Environ. Sci. Dev. 7 (2016) 646–650 https://doi.org/10.18178/ijesd.2016.7.9.855.
[31] H. Chen, D. Zhou, G. Luo, S. Zhang, J. Chen, Macroalgae for biofuels production: progress and perspectives, Renew. Sust. Energ. Rev. 47 (2015) 427–437, https://doi.org/10.1016/j.rser.2015.03.086.
[32] S. Lordan, R.P. Ross, C. Stanton, Marine bioactives as functional food ingredients: potential to reduce the incidence of chronic diseases, Mar. Drugs 9 (2011) 1056–1100, https://doi.org/10.3390/md9061056.
[33] K. Anastasakis, A.B. Ross, J.M. Jones, Pyrolysis behaviour of the main carbohydrates of brown macro-algae, Fuel 90 (2011) 598–607, https://doi.org/10.1016/j.fuel.2010.09.023.
[34] G. Michel, T. Tonon, D. Scornet, J.M. Cock, B. Kloareg, The cell wall polysaccharide metabolism of the brown alga Ectocarpus siliculosus. Insights into the evolution of extracellular matrix polysaccharides in eukaryotes, New Phytol. 188 (2010) 82–97, https://doi.org/10.1111/j.1469-8137.2010.03374.x.
[35] S.J. Horn, I.M. Aasen, K. Østgaard, Production of ethanol from mannitol by Zymobacter palmae, J. Ind. Microbiol. Biotechnol. 24 (2000) 51–57, https://doi.org/10.1038/sj.jim.2900771.
[36] S.U. Kadam, B.K. Tiwari, C.P. O'Donnell, Extraction, structure and biofunctional activities of laminarin from brown algae, Int. J. Food Sci. Technol. 50 (2015) 24–31, https://doi.org/10.1111/ijfs.12692.
[37] J.M. Adams, J.A. Gallagher, I.S. Donnison, Fermentation study on Saccharina latissima for bioethanol production considering variable pretreatments, J. Appl. Phycol. 21 (2009) 569–574, https://doi.org/10.1007/s10811-008-9384-7.
[38] R.P. John, G.S. Anisha, K.M. Nampoothiri, A. Pandey, Micro and macroalgal biomass: a renewable source for bioethanol, Bioresour. Technol. 102 (2011) 186–193, https://doi.org/10.1016/j.biortech.2010.06.139.
[39] H.R. Fletcher, P. Biller, A.B. Ross, J.M.M. Adams, The seasonal variation of fucoidan within three species of brown macroalgae, Algal Res. 22 (2017) 79–86, https://doi.org/10.1016/j.algal.2016.10.015.
[40] S.R. Sivakumar, K. Arunkumar, Sodium, potassium and sulphate composition in some seaweeds occurring along the coast of Gulf of Mannar, India, Asian J. Plant Sci. 8 (2009) 500–504, https://doi.org/10.3923/ajps.2009.500.504.
[41] E.D. Obluchinskaya, Comparative chemical composition of the Barents Sea brown algae, Appl. Biochem. Microbiol. 44 (2008) 305–309, https://doi.org/10.1134/S0003683808030149.
[42] P. Bohutskyi, E. Bouwer, Biogas production from algae and cyanobacteria through anaerobic digestion: a review, analysis, and research needs, in: J.W. Lee (Ed.), Characterization of Biochars Using Advanced Solid-State 13°C Nuclear Magnetic Resonance Spectroscopy, Springer, New York, 2013, pp. 873–975, , https://doi.org/10.1007/978-1-4614-3348-4_36.
[43] F. Passos, E. Uggetti, H. Carrère, I. Ferrer, Pretreatment of microalgae to improve biogas production: a review, Bioresour. Technol. 172 (2014) 403–412, https://doi.org/10.1016/j.biortech.2014.08.114.
[44] M.E. Montingelli, K.Y. Benyounis, J. Stokes, A.G. Olabi, Pretreatment of macroalgal biomass for biogas production, Energy Convers. Manag. 108 (2016) 202–209, https://doi.org/10.1016/j.enconman.2015.11.008.
[45] J. Ariunbaatar, A. Panico, G. Esposito, F. Pirozzi, P.N.L. Lens, Pretreatment methods to enhance anaerobic digestion of organic solid waste, Appl. Energ. 123 (2014) 143–156, https://doi.org/10.1016/j.apenergy.2014.02.035.
[46] C. Rodriguez, A. Alaswad, J. Mooney, T. Prescott, A.G. Olabi, Pretreatment techniques used for anaerobic digestion of algae, Fuel Process. Technol. 138 (2015) 765–779, https://doi.org/10.1016/j.fuproc.2015.06.027.
[47] G. Zhen, X. Lu, T. Kobayashi, Y.-Y. Li, K. Xu, Y. Zhao, Mesophilic anaerobic co-

digestion of waste activated sludge and Egeria densa: performance assessment and kinetic analysis, Appl. Energ. 148 (2015) 78–86, https://doi.org/10.1016/j.apenergy.2015.03.038.
[48] L. Kratky, T. Jirout, Biomass size reduction machines for enhancing biogas production, Chem. Eng. Technol. 34 (2011) 391–399, https://doi.org/10.1002/ceat.201000357.
[49] A.J. Ward, D.M. Lewis, F.B. Green, Anaerobic digestion of algae biomass: a review, Algal Res. 5 (2014) 204–214, https://doi.org/10.1016/j.algal.2014.02.001.
[50] S. Tedesco, T.M. Barroso, A. Olabi, Optimization of mechanical pretreatment of Laminariaceae spp. biomass-derived biogas, Renew. Energ. 62 (2014) 527–534, https://doi.org/10.1016/j.renene.2013.08.023.
[51] G.G.D. Silva, M. Couturier, J.-G. Berrin, A. Buléon, X. Rouau, Effects of grinding processes on enzymatic degradation of wheat straw, Bioresour. Technol. 103 (2012) 192–200, https://doi.org/10.1016/j.biortech.2011.09.073.
[52] M. Carlsson, A. Lagerkvist, F. Morgan-Sagastume, The effects of substrate pretreatment on anaerobic digestion systems: a review, Waste Manag. 32 (2012) 1634–1650, https://doi.org/10.1016/j.wasman.2012.04.016.
[53] C. Rodriguez, A. Alaswad, Z. El-Hassan, A.G. Olabi, Improvement of methane production from P. canaliculata through mechanical pretreatment, Renew. Energ. 119 (2018) 73–78, https://doi.org/10.1016/j.renene.2017.12.025.
[54] H.B. Nielsen, S. Heiske, Anaerobic digestion of macroalgae: methane potentials, pretreatment, inhibition and co-digestion, Water Sci. Technol. 64 (2011) 1723–1729, https://doi.org/10.2166/wst.2011.654.
[55] J. Kim, G. Yoo, H. Lee, J. Lim, K. Kim, C.W. Kim, et al., Methods of downstream processing for the production of biodiesel from microalgae, Biotechnol. Adv. 31 (2013) 862–876, https://doi.org/10.1016/j.biotechadv.2013.04.006.
[56] R.U. Rani, S.A. Kumar, S. Kaliappan, I. Yeom, J.R. Banu, Impacts of microwave pretreatments on the semi-continuous anaerobic digestion of dairy waste activated sludge, Waste Manag. 33 (2013) 1119–1127, https://doi.org/10.1016/j.wasman.2013.01.016.
[57] E. Vázquez-Delfín, D. Robledo, Y. Freile-Pelegrín, Microwave-assisted extraction of the carrageenan from Hypnea musciformis (Cystocloniaceae, Rhodophyta), J. Appl. Phycol. 26 (2014) 901–907, https://doi.org/10.1007/s10811-013-0090-8.
[58] M.E. Alzate, R. Muñoz, F. Rogalla, F. Fdz-Polanco, S.I. Pérez-Elvira, Biochemical methane potential of microalgae: influence of substrate to inoculum ratio, biomass concentration and pretreatment, Bioresour. Technol. 123 (2012) 488–494, https://doi.org/10.1016/j.biortech.2012.06.113.
[59] F. Passos, J. Carretero, I. Ferrer, Comparing pretreatment methods for improving microalgae anaerobic digestion: thermal, hydrothermal, microwave and ultrasound, Chem. Eng. J. 279 (2015) 667–672, https://doi.org/10.1016/j.cej.2015.05.065.
[60] K.Y. Park, J. Kweon, P. Chantrasakdakul, K. Lee, H.Y. Cha, Anaerobic digestion of microalgal biomass with ultrasonic disintegration, Int. Biodeterior. Biodegradation 85 (2013) 598–602, https://doi.org/10.1016/j.ibiod.2013.03.035.
[61] C. González-Fernández, B. Sialve, N. Bernet, J.P. Steyer, Comparison of ultrasound and thermal pretreatment of Scenedesmus biomass on methane production, Bioresour. Technol. 110 (2012) 610–616, https://doi.org/10.1016/j.biortech.2012.01.043.
[62] F. Passos, S. Astals, I. Ferrer, Anaerobic digestion of microalgal biomass after ultrasound pretreatment, Waste Manag. 34 (2014) 2098–2103, https://doi.org/10.1016/j.wasman.2014.06.004.
[63] S. Cho, S. Park, J. Seon, J. Yu, T. Lee, Evaluation of thermal, ultrasonic and alkali pretreatments on mixed-microalgal biomass to enhance anaerobic methane production, Bioresour. Technol. 143 (2013) 330–336, https://doi.org/10.1016/j.biortech.2013.06.017.
[64] S.U. Kadam, C.P. O'Donnell, D.K. Rai, M.B. Hossain, C.M. Burgess, D. Walsh, et al., Laminarin from Irish brown seaweeds Ascophyllum nodosum and Laminaria hyperborea: ultrasound assisted extraction, characterization and bioactivity, Mar. Drugs 13 (2015) 4270–4280, https://doi.org/10.3390/md13074270.
[65] T. Hahn, S. Lang, R. Ulber, K. Muffler, Novel procedures for the extraction of fucoidan from brown algae, Process Biochem. 47 (2012) 1691–1698, https://doi.org/10.1016/j.procbio.2012.06.016.
[66] C. Rodriguez, A. Alaswad, K. Benyounis, A. Olabi, Pretreatment techniques used in biogas production from grass, Renew. Sust. Energ. Rev. 68 (2017) 1193–1204, https://doi.org/10.1016/j.rser.2016.02.022.
[67] S. Tedesco, K.Y. Benyounis, A.G. Olabi, Mechanical pretreatment effects on macroalgae-derived biogas production in co-digestion with sludge in Ireland, Energy 61 (2013) 27–33, https://doi.org/10.1016/j.energy.2013.01.071.
[68] L. Pastare, I. Aleksandrovs, D. Lauka, F. Romagnoli, Mechanical pretreatment effect on biological methane potential from marine macro algae: results from batch tests of Fucus vesiculosus, Energy Procedia 95 (2016) 351–357, https://doi.org/10.1016/j.egypro.2016.09.021.
[69] H. Li, H. Kjerstadius, E. Tjernström, Å. Davidsson, Evaluation of pretreatment methods for increased biogas production from macro algae. Svenskt Gastekniskt Center AB, SGC RAPPORT. 278. http://www.sgc.se/ckfinder/userfiles/files/SGC278.pdf, 2013 (accessed 11 November 2018).
[70] R. Sindhu, P. Binod, A. Pandey, Biological pretreatment of lignocellulosic biomass – an overview, Bioresour. Technol. 199 (2016) 76–82, https://doi.org/10.1016/j.biortech.2015.08.030.
[71] Isroi, R. Millati, S. Syamsiah, C. Niklasson, M.N. Cahyanto, K. Lundquist et al., Biological pretreatment of lignocelluloses with white-rot fungi and its applications: a review, Bio Resources 6 (2011) 5224–5259. https://www.scopus.com/inward/record. uri? eid = 2-s2.0–84856499379& partner ID = 40& md 5 = fab 7e256b104fcbea56e23e1a245d680.
[72] X. Zhang, H. Yu, H. Huang, Y. Liu, Evaluation of biological pretreatment with white rot fungi for the enzymatic hydrolysis of bamboo culms, Int. Biodeterior. Biodegradation 60 (2007) 159–164, https://doi.org/10.1016/j.ibiod.2007.02.003.
[73] R. Tapia-Tussell, J. Avila-Arias, J.D. Maldonado, D. Valero, E. Olguin-Maciel, D. Pérez-Brito, et al., Biological pretreatment of Mexican Caribbean macroalgae consortiums using Bm-2 Strain (Trametes hirsuta) and its enzymatic broth to improve biomethane potential, Energies 11 (2018) 494, https://doi.org/10.3390/en11030494.
[74] C. Vanegas, A. Hernon, J. Bartlett, Enzymatic and organic acid pretreatment of seaweed: effect on reducing sugars production and on biogas inhibition, Int. J. Ambient Energy 36 (2015) 2–7, https://doi.org/10.1080/01430750.2013.820143.
[75] M.D. Marsolek, E. Kendall, P.L. Thompson, T.R. Shuman, Thermal pretreatment of algae for anaerobic digestion, Bioresour. Technol. 151 (2014) 373–377, https://doi.org/10.1016/j.biortech.2013.09.121.
[76] J.C. Costa, J.V. Oliveira, M.A. Pereira, M.M. Alves, A.A. Abreu, Biohythane production from marine macroalgae Sargassum sp. coupling dark fermentation and anaerobic digestion, Bioresour. Technol. 190 (2015) 251–256, https://doi.org/10.1016/j.biortech.2015.04.052.
[77] A. Yousefifar, S. Baroutian, M.M. Farid, D.J. Gapes, B.R. Young, Fundamental mechanisms and reactions in non-catalytic subcritical hydrothermal processes: a review, Water Res. 123 (2017) 607–622, https://doi.org/10.1016/j.watres.2017.06.069.
[78] C.K. Nitsos, K.A. Matis, K.S. Triantafyllidis, Optimization of hydrothermal pretreatment of lignocellulosic biomass in the bioethanol production process, Chem Sus Chem 6 (2013) 110–122, https://doi.org/10.1002/cssc.201200546.
[79] B. Yang, L. Tao, C.E. Wyman, Strengths, challenges, and opportunities for hydrothermal pretreatment in lignocellulosic biorefineries, Biofuels Bioprod. Biorefin. 12 (2018) 125–138, https://doi.org/10.1002/bbb.1825.
[80] A.G. Carr, R. Mammucari, N.R. Foster, A review of subcritical water as a solvent and its utilisation for the processing of hydrophobic organic compounds, Chem. Eng. J. 172 (2011) 1–17, https://doi.org/10.1016/j.cej.2011.06.007.
[81] B. Patel, M. Guo, A. Izadpanah, N. Shah, K. Hellgardt, A review on hydrothermal pretreatment technologies and environmental profiles of algal biomass processing, Bioresour. Technol. 199 (2016) 288–299, https://doi.org/10.1016/j.biortech.2015.09.064.
[82] K. Hii, S. Baroutian, R. Parthasarathy, D.J. Gapes, N. Eshtiaghi, A review of wet air oxidation and thermal hydrolysis technologies in sludge treatment, Bioresour. Technol. 155 (2014) 289–299, https://doi.org/10.1016/j.biortech.2013.12.066.
[83] P. Yazdani, A. Zamani, K. Karimi, M.J. Taherzadeh, Characterization of Nizimuddinia zanardini macroalgae biomass composition and its potential for biofuel production, Bioresour. Technol. 176 (2015) 196–202, https://doi.org/10.1016/j.biortech.2014.10.141.
[84] Y.N. Barbot, L. Thomsen, R. Benz, Thermo-acidic pretreatment of beach macroalgae from Rügen to optimize biomethane production - double benefit with simultaneous bioenergy production and improvement of local beach and waste management, Mar. Drugs 13 (2015) 5681–5705, https://doi.org/10.3390/md13095681.
[85] Y.N. Barbot, H.M. Falk, R. Benz, Thermo-acidic pretreatment of marine brown algae Fucus vesiculosus to increase methane production - a disposal principle for macroalgae waste from beaches, J. Appl. Phycol. 27 (2015) 601–609, https://doi.org/10.1007/s10811-014-0339-x.
[86] Y. Yin, J. Wang, Pretreatment of macroalgal Laminaria japonica by combined microwave-acid method for biohydrogen production, Bioresour. Technol. 268 (2018) 52–59, https://doi.org/10.1016/j.biortech.2018.07.126.
[87] T. Eggeman, R.T. Elander, Process and economic analysis of pretreatment technologies, Bioresour. Technol. 96 (2005) 2019–2025, https://doi.org/10.1016/j.biortech.2005.01.017.
[88] S. Perez-Elvira, M. Fdz-Polanco, F.I. Plaza, G. Garralon, F. Fdz-Polanco, Ultrasound pretreatment for anaerobic digestion improvement, Water Sci. Technol. 60 (2009) 1525–1532, https://doi.org/10.2166/wst.2009.484.
[89] C. Rodriguez, A. Alaswad, Z. El-Hassan, A.G. Olabi, Mechanical pretreatment of waste paper for biogas production, Waste Manag. 68 (2017) 157–164, https://doi.org/10.1016/j.wasman.2017.06.040.
[90] P. Kumar, D.M. Barrett, M.J. Delwiche, P. Stroeve, Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production, Ind. Eng. Chem. Res. 48 (2009) 3713–3729, https://doi.org/10.1021/ie801542g.
[91] J.A. Muller, Prospects and problems of sludge pretreatment processes, Water Sci. Technol. 44 (2001) 121–128, https://doi.org/10.2166/wst.2001.0598.
[92] N.R. Baral, A. Shah, Comparative techno-economic analysis of steam explosion, dilute sulfuric acid, ammonia fiber explosion and biological pretreatments of corn Stover, Bioresour. Technol. 232 (2017) 331–343, https://doi.org/10.1016/j.biortech.2017.02.068.
[93] F.K. Kazi, J.A. Fortman, R.P. Anex, D.D. Hsu, A. Aden, A. Dutta, et al., Techno-economic comparison of process technologies for biochemical ethanol production from corn stover, Fuel 89 (2010) S20–S28, https://doi.org/10.1016/j.fuel.2010.01.001.
[94] F. Passos, V. Ortega, A. Donoso-Bravo, Thermochemical pretreatment and anaerobic digestion of dairy cow manure: experimental and economic evaluation, Bioresour. Technol. 227 (2017) 239–246, https://doi.org/10.1016/j.biortech.2016.12.034.
[95] É.L. Bordeleau, R.L. Droste, Comprehensive review and compilation of pretreatments for mesophilic and thermophilic anaerobic digestion, Water Sci. Technol. 63 (2011) 291–296, https://doi.org/10.2166/wst.2011.052.
[96] S.S. Mansouri, I.A. Udugama, S. Cignitti, A. Mitic, X. Flores-Alsina, K.V. Gernaey, Resource recovery from bio-based production processes: a future necessity? Curr. Opin. Chem. Eng. 18 (2017) 1–9, https://doi.org/10.1016/j.coche.2017.06.002.

[97] I.A. Udugama, S.S. Mansouri, A. Mitic, X. Flores-Alsina, K.V. Gernaey, Perspectives on resource recovery from bio-based production processes: from concept to implementation, Processes 5 (2017) 48, https://doi.org/10.3390/pr5030048.
[98] Y. Shen, J.L. Linville, M. Urgun-Demirtas, M.M. Mintz, S.W. Snyder, An overview of biogas production and utilization at full-scale wastewater treatment plants (WWTPs) in the United States: challenges and opportunities towards energy-neutral WWTPs, Renew. Sust. Energ. Rev. 50 (2015) 346–362, https://doi.org/10.1016/j.rser.2015.04.129.
[99] Cambi, Cambi solid stream - high dry solids technology, http://www.sbhub.se/file/dokument/seminariepresentationer-2016/gasseminarium/sandbackathermal-hydrolysis. pdf, 2016 (accessed 26 November 2018).
[100] Cambi, Cambi Thermal Hydrolysis from Waste to Worth, http://www.razemdlaklimatu.eu/images/2016/20160926/prezentacje/Hydroliza_termiczna_w_technologii_CAMBI.pdf, (2016) , Accessed date: 26 November 2018.
[101] Cambi, Cambi thermal hydrolysis theory, market and the future, https://www.wef.org/globalassets/assets-wef/3—resources/online-education/eshowcases/handouts/presentation-handouts—cambi-eshowcase-2.pdf, (2016) , Accessed date: 26 November 2018.
[102] Cambi, Cambi contribution to circular economy, http://www.chimicaverdelombardia.it/wp-content/uploads/2019/06/Cambi_Ferraro.pdf, (2019) , Accessed date: 25 June 2019.
[103] L. Menco, Cambi thermal hydrolysis sludge treatment: medium to large-scale application, http://www.environmentindex.com/en/article/cambi-thermal-hydrolysis-sludge-treatment-medium-to-large-scale-application-677.aspx, (2012) , Accessed date: 28 November 2018.
[104] Cambi, Cambi thermal hydrolysis, http://nesowea.org/wp-content/uploads/2015/08/09a-Astbury-OWEA-Cambi-Presentation.pdf, (2015).
[105] A.B. Cooper, L. Benson, W. Bailey, E. Jolly, W. Krill, Maximizing benefits from renewable energy at Blue Plains AWWTP, https://isr.umd.edu/~adomaiti/chbe446/CooperKrill2010.pdf, (2010) , Accessed date: 26 November 2018.