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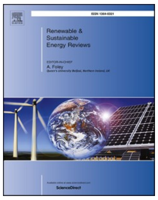

Pelagic *Sargassum* for energy and fertiliser production in the Caribbean: A case study on Barbados

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ABSTRACT

In recent years pelagic *Sargassum* has invaded the coastlines of the Caribbean region, Gulf of Mexico, Florida and West Africa, triggering human health concerns and negatively impacting environmental and economic productivity. *Sargassaceae* are nutrient-dense and currently utilized as fertiliser and food, while extracts of their phytochemicals exhibit unique biosorption and medicinal properties. This macroalgae also shows biofuel potential but hitherto, methane recovery is low due to a carbon to nitrogen ratio below 20:1, the restricted bioavailability of structurally complex carbohydrates for degradation and high insoluble fibre, salt, polyphenol and sulfur content. To optimise the microbial bioconversion of this biomass, pre-treatment and co-fermentation with other substrates have been explored. This paper reviews the challenges associated with, and potential solutions for, *Sargassum* inundation, and provides a critical evaluation of its bioconversion to biogas and fertiliser using anaerobic digestion technology. As the Caribbean region is primarily impacted by drifting *Sargassum* blooms, the paper concludes with a case study on Barbados and investigates the feasibility of repurposing this brown macroalgae from landfill disposal to a feedstock for electricity and fertiliser production. The results of this study indicate that *Sargassum* mono-digestion is unsustainable for energy extraction given its low bioconversion efficiency and unpredictable influx volume. Alternatively, the co-digestion of these seaweeds with organic municipal solid waste is economically and energetically advantageous, potentially enhancing energy recovery by 5-fold. Notably, the hydrogen sulfide fraction of the biogas generated must be controlled given its corrosive properties and potential to effect co-generation engine damage and failure. Additional income can also be derived through the agricultural application of the digestate generated both locally and externally, following ammonia treatment and heavy metal stripping. Further research and pilot-scale studies are therefore necessary to support the utilisation of this marine biomass in commercial energy and fertiliser production.

1. Introduction

The past eight years saw the coastlines of the Caribbean region inundated with the pelagic seaweed *Sargassum*, which enters regional waters annually and accumulates, before washing ashore. Present in large quantities and emitting noxious hydrogen sulfide upon decomposition, *Sargassum* influx has impeded the growth of regional tourism and fisheries sectors. Moreover, its frequent and abundant reoccurrence has devastated and rendered vulnerable Caribbean economies which depend on these sectors for survival [1]. Sir Hilary Beckles, Vice Chancellor of the University of the West Indies, was therefore apt in his description of *Sargassum* in 2015, as "the greatest single threat" to the Caribbean. While several forums, including the "*Sargassum* Symposium" have been created to examine *Sargassum*-impact mitigation strategies across the Caribbean region, an urgent transition from proposal to technology implementation is now required to ensure coastal and economic sustainability [2].

Sargassum, named after the Sargasso Sea in the North Atlantic Ocean, is a genus of brown macro-algae. This aquatic biomass sits on the surface of the ocean where it amalgamates into long algal mats and drifts with ocean currents. Annually, the Sargasso Sea accommodates approximately 4–10 megatonnes of over 100 species of *Sargassum* seaweed [3]. However, the *Sargassum* composition of the Sargasso Sea is dominated by the two species *S. natans* and *S. fluitans* which collectively represent 90% of the macro-algal population [4]. Differing solely in pod and leaf morphology, these two species contain gas-filled bladders which render them holopelagic, thus facilitating growth that is entirely independent of ocean floor attachment and reproduction via fragmentation [5].

In nature, *Sargassum* blooms provide a habitat to over 127 species of

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Abbreviations

AD	Anaerobic digestion
BBD	Barbados dollar
BLPC	Barbados Light and Power Company
BMP	Biochemical methane potential
C&D	Construction and demolition
C:N	Carbon to nitrogen ratio
COD	Chemical oxygen demand
dw	Dry weight
FW	Food waste
GAE	Gallic acid equivalents
GDP	Gross domestic product
GOB	Government of Barbados
GWh	Gigawatt hours
kWh	Kilowatt hours
MERIS	Medium Resolution Imaging Spectrometer
MW	Megawatts
MWh	Megawatt hours
NERR	North Equatorial Recirculation Region
OMSW	Organic municipal solid waste
OLR	Organic loading rate
SBRC	Sustainable Barbados Recycling Centre
SMY	Specific methane yield
TMP	Theoretical methane potential
TS	Total solids
VFA	Volatile fatty acids
VS	Volatile solids

fish and 145 invertebrates, several of which are threatened and endangered. These seaweeds also contribute significantly to environmental stability, enabling the Sargasso Sea to sequester approximately 7% of the global net carbon emissions annually [3,6].

Across the North Atlantic Ocean, *Sargassum* growth has been exponential for the past three decades. However, uncertainty remains surrounding the origin and circulatory patterns of this marine biomass in the Atlantic Ocean. Satellite images taken from the Medium Resolution Imaging Spectrometer (MERIS) for the period 2002 to 2008 reveal the annual growth of 1 megatonne of *Sargassum* in the north western Gulf of Mexico [7]. This seaweed translocates along the Florida Straits into the Sargasso Sea where it proliferates during the spring and summer months [7,8], doubling in mass in these oceanic waters every 50 d [9,10]. The North Equatorial Recirculation Region (NERR), which is northeast of Brazil is also identified as a secondary growth site of Atlantic *Sargassum* blooms [11].

While the primary cause of increased *Sargassum* spawning is undetermined, this phenomenon has been linked to climate change and eutrophication. The steady upsurge in global carbon-dioxide levels effected by climate change has promoted ocean acidification and sea temperature increase [5,12]. These conditions enhance both macro-algal photosynthetic efficiency and the uptake of essential nutrients from the excretions of the fish inhabiting these algal blooms [10]. African dust emanating from the Sahara Desert has also been linked to *Sargassum* growth in the tropical North Atlantic [11].

In the NERR, *Sargassum* proliferation is further accelerated by the nutrient-dense discharges of the Orinoco, Congo and Amazon rivers, the latter being the primary nutrient source, considering the strong linkage between peak emissions and years of Atlantic Ocean algal bloom. The Amazon river is enriched with nitrates and phosphates supplied by the continental run-off of deforestation, agro-industrial and urban sources [11]. This variable renders the NERR more fertile than the Sargasso Sea, doubling *Sargassum* growth in the neritic zone every 11 d [9,10].

Distribution mapping of drifting *Sargassum* blooms over the last 15 years reveal increased algal spread across the Central West Atlantic commencing in 2011 [13]. Comparison of *Sargassum* sampled from the Sargasso Sea and the Caribbean region in 2014/2015 reflect differences in its morphology at the two locations [14]. Therefore, the NERR is considered responsible for the unprecedented level of algal inundation experienced in the Caribbean and West Africa within recent years [9,11].

Globally, the response to *Sargassum* inundation events has been measured due to the absence of robust detection and monitoring systems [15]. In 2015, the Caribbean recorded a peak daily influx of 10,000 tonnes (t) of *Sargassum* [1] which represents a 20-fold increase in mass relative to the years preceding 2010 [13]. During the same period, the Mexican Caribbean coast received on average 2360 m^3 of *Sargassum* per km of coastline [15]. Beach-cast *Sargassum* is generally removed and disposed of through landfilling [14].

The *Sargassaceae* family exhibits application as a horticultural stimulant [16], food supplement [16,17], heavy metal biosorber [18] and medical phytochemical source [19,20]. Researchers have also explored the valorisation of this genus into biofuels [3,21]. However, a compilation of past and present studies on this topic has highlighted a critical knowledge gap in the methanation of pelagic *Sargassum* blooms. To date, a single report exists on the potential use of these seaweeds for energy production in Grenada and St. Lucia [22]. Further research on anaerobic digestion (AD) of this marine biomass is necessary to provide authorities in *Sargassum*-impacted territories with an eco-friendly and economically viable solution to its recurring influx.

This study provides an overview of the negative impact of *Sargassum* inundation on Caribbean economies and highlights the current and potential applications of this marine biomass, with emphasis placed on biogas and fertiliser production through AD. A case study on Barbados is presented to examine the feasibility of utilising these seaweeds as feedstock for energy and fertiliser production. Implications for policy development, commercialisation and future research are also discussed.

2. Issues with *Sargassum* influx

The annual migration of small quantities of *Sargassum* into coastlines of the Caribbean region is a natural process. These small deposits are beneficial as the fortification and stabilization of sandbanks against wave and hurricane-force winds [23]. In addition, this biomass provides nutrients and a habitat to foraging invertebrates [3]. However, the massive influx, consolidation and subsequent decay of pelagic seaweed in the neritic zone and along Caribbean shorelines have devastated coastal ecosystems and regional economies.

2.1. Marine ecosystem

Coral reefs located on the ocean floor in tropical waters maintain oceanic biodiversity by hosting hundreds of marine organisms [24]. However, within the past two decades, modifications to oceanic conditions effected by higher anthropogenic levels have triggered an ecological phase shift away from coral formation towards copious macro-algae spread [25]. Coral and macro-algae exhibit a parasitic relationship and exposure between the two entities promotes coral bleaching and reef mortality [26]. Hitherto, 20% of the global coral reef population has been lost and approximately 30% of that remaining is endangered [24]. In the Caribbean, 80% of coral reefs have been destroyed over the last 50 years [27]. Restoration of this fragile ecosystem is maintained by herbivorous fish which forage on seaweeds [28,29].

Sea turtles are macro-herbivores hosted in and protected by *Sargassum* from the Sargasso Sea. These reptiles find nourishment in algal blooms and use them to translocate across the waters of the North Atlantic Ocean for nesting and breeding [30] as evident when tracked by satellite [31]. However, once ashore, nesting is impaired by the new phenomenon of mass *Sargassum* accumulation on beaches and along shallow coastlines [32]. While some turtles may competently traverse the macro-algal build-up pre and post nesting, this is inconsistent as in 2015, entrapment led to the death of 42 Hawksbill turtles on Long Beach, Barbados [33]. Sea turtles generally return to their hatching site to nest and any obstructions experienced during this process, result in the abortion of that nesting season and ultimately reduce future generations [32].

2.2. *Fishing industry*

The Caribbean region depends heavily on the annual migration of shoals of fish with *Sargassum* across the North Atlantic Ocean into its waters. For example, in the island of Barbados, fisheries generate US $14.6 M annually, a contribution of 0.3% to the gross domestic product (GDP) [34]. However, the new phenomena of *Sargassum* influx into the Caribbean has triggered a state of emergency in the fisheries sector of several islands. During periods of inundation, fisher-folk reported reduced visibility, higher occurrences of fishing net entanglement, widespread boat damage and lower fish capture [16,35]. Several Caribbean islands have also observed the surfacing of hundreds of dead fish along their inundated coastlines, a problem attributed to the de-oxygenation of littoral waters by decomposing *Sargassum* and the oceanic release of toxic chemicals by floating *Sargassum* [36].

2.3. *Tourism industry*

Tourism is the major sector in most countries in the Caribbean region, accounting for more than 80% of the annual GDP [3]. In 2017, direct contributions from this industry to Caribbean economies were US $57.1 B, with a projected increase to US $83.3 B by 2027 [37]. The growth of this sector depends heavily on beach-front beauty and friendliness. It is therefore understandable that in 2015, the pungent smells and grotesque nature of decomposing beach-cast *Sargassum*, coupled with the attracted flies, drew extensive, negative international media coverage and contributed to increased tourist cancellations and reduced arrivals to the Caribbean region [38,39]. Human health and infrastructural integrity have also been compromised by the hydrogen sulfide emitted during *Sargassum* decomposition [16,39]. Regrettably, the cost of coastal restoration is exorbitant, estimated at US $120 M in the Caribbean region alone [2]. In Mexico, the restoration of the beaches on the Quintana Roo coast totalled US $9.1 M and utilized 5000 labourers [14,38,40]. Alternative collection mechanisms include the deployment of an ocean surface rig in the Dominican Republic [41] and the installation of Green Brigades in Guadeloupe [42].

3. Current and potential applications of *Sargassum*

3.1. *Fertiliser*

Sargassum is widely regarded as a bio-fertiliser in agriculture [16]. This nutrient-dense macroalgae is rich in minerals, water soluble polysaccharides and phenolic compounds which collectively enhance soil health, quality, productivity and enzymatic activities [43]. Consequently, the growth rates and yields of crops exposed to this natural fertiliser are higher than those achieved with traditional chemical fertilisers [16,44].

The application of *S. johnstonii* to soil increased the organic composition and essential minerals levels (Na, Mg, K, Ca and Zn) of the soil by more than 100-fold. Water retention and soil structure were also improved. These amended soil conditions promoted the overall growth and early flowering and fruiting of tomato plants compared to unfertilised crops [45,46]. Similarly, Indian *Vigna mungo* seedling growth rose by 4% following incubation in 10% liquefied *S. myriocystum* extract for 24 h. Relative to the control, addition of this macro-algal extract to the growth medium increased the shoot and root length from 15.4 to 21.1 cm and 6.8–12.2 cm per seedling, respectively [47].

Williams and Feagin [23] also reported the positive growth response of dune plants to *Sargassum*-enriched soil. In this study, unwashed *Sargassum* proved most effective at increasing overall plant growth and development. Application of the biomass in its raw state promoted maximum absorption of essential soluble macro-algal nutrients, which were otherwise leached from the seaweed when washed. Chemical analysis of rinsed *Sargassum* samples confirmed the depletion of N, Na and P, while elevated levels of these essential growth nutrients were measured in the rinse water. The reduced demand for a processing or washing phase therefore renders the direct application of *Sargassum* to soil an economical fertiliser [23]. Noteworthy, the salinity of unwashed *Sargassum* must be monitored as it can create osmotic stress which obstructs seedling water uptake and crop productivity [48].

3.2. *Food products*

Human consumption of seaweeds has increased over the last decade. In 2014, this market was valued at US $5.5 B, rising 2-fold to US $11 B in 2016 [22]. Brown macro-algae are edible and consumed across Asia and Europe as a natural and healthy alternative to traditional foods. These nutrient-dense seaweeds can be consumed raw or added to food products to improve their nutritional composition, shelf-life and health properties [49,50].

In Japan, 10% of the daily dietary needs are meet by *Sargassum*. These seaweeds are rich in dietary fibre and are ingested in their raw form or added to soups [16,17]. Dietary fibre aids digestion and colonic health while mitigating coronary disease. The daily fibre requirement in the human diet is 24 g. *Sargassum* spp. possess more fibre than traditional whole foods such as brown rice (3.8 g/100 g weight) and lentil peas (8.9 g/100 g weight). The consumption of 8 g of this algae would therefore satisfy one-eighth (12.5%) of the daily fibre demand [50].

The lipid content of *Sargassum* spp. is low with a fatty acid profile consisting of saturated, monounsaturated and polyunsaturated fatty acids, the latter of which is most abundant [51]. The polyunsaturated fatty acid fraction varies in ratio from 0.5:1 to 3:1 of omega-6 to omega-3 lipids [46]. These ratios are within the stipulated maximum of 10:1 and justify the use of these seaweeds in dietary supplements which support cardio-vascular health [52].

Sargassum spp. are enriched with protein and a polysaccharide fraction composed mainly of laminarin, mannitol, fucoidan and alginate [53]. Seaweeds enriched with carbohydrates exhibit potential application in bread making. The incorporation of this marine biomass into flour enhances the structural dynamics and water retention capacity of the dough. Moreover, the nutritional content and firmness of the resulting bread products are improved [54]. Alginates are also extractable and can be added to food as gelling, thickening, encapsulating and coating agents [55].

The high ash levels of *Sargassum* spp. reflect the presence of large quantities of essential macro-minerals and vitamins, all important components of a balanced human diet [56]. Table 1 shows the nutritional composition of several *Sargassum* sp. sampled from various locations world-wide.

3.3. *Biosorption*

Biomass biosorption of heavy metals is being explored as a cost-effective alternative to conventional biosorption technologies. Heavy metals are industrially-produced high density elements, which are detrimental to human and environmental health when emitted into the atmosphere. The swift removal of these toxic particulates is therefore paramount to mitigate their harmful effect [63].

Brown seaweeds show great potential as economic and

Table 1
Proximate composition of various *Sargassum* spp.

Species	Harvesting point	Sample season	Drying conditions	Carbohydrates*	Protein*	Lipids*	Total Fibre*	Ash*	Ref.
S. vulgare	Brazil	–	oven-dried at 50 °C	67.8	15.8	0.5	7.7	14.2	[57]
S. hemiphyllum	Hong Kong	Winter	sun-dried for 4 d	–	10.1	3.0	62.9	19.6	[58]
			oven-dried at 60 °C	–	9.8	3.4	56.8	21.5	
			freeze-dried at −70 °C	–	10.0	4.4	60.2	21.1	
S. polycystum	North Borneo	–	freeze-dried at −20 °C	33.5	5.4	0.3	39.7	42.4	[59]
S. platycarpum	Puerto Rico and U.S. Virgin Islands	Spring	oven-dried at – 75 °C	48.7	6.9	0.4	8.0	36.8	[60]
S. rigidulum				44.8	5.9	0.4	8.2	40.7	
S. lendigerum				41.6	6.4	0.5	7.9	43.7	
S. mangarevense	Tahiti	Summer	oven-dried at 60 °C	–	13.2	3.4	42.8	30.6	[61]
S. muticum	Portugal	Spring	oven-dried at 60 °C	49.3	16.9	1.45	–	22.94	[62]
S. polyschides				45.6	14.4	1.1	–	28.15	

* Values are expressed as percentage (%) dw.

environmentally-friendly biosorption media, because of their high cell wall alginate content. Compared to other genera, *Sargassum* exhibit a higher metal-binding capacity effected by the presence of sulfonate groups and a unique composition of alginates [18,63]. These properties contributed to the successful removal of Pb, Cu, Zn and Mn from multi-solute solutions and real urban storm water run-off [64]. The Sargassum genus exhibits a high affinity for Pb with 90% total metal ion recovery achieved from aqueous solutions. In this work, the maximum uptake capacities recorded were 1.16, 0.99, 0.76, 0.61 and 0.50 mmoL/g for Pb, Cu, Cd, Zn and Ni, respectively, over 60 min [65]. Cd binding is also important as this heavy metal ranks in the top three of the most harmfully produced emittances in industry [18].

Heavy metal removal can however be impaired by the high salinity of *Sargassum* spp. Patrón-Prado et al. [66] observed reduced wastewater heavy metal binding by *S. sinicola* as the salt concentration increased from 0 to 5.8 practical salinity units. This change in the salt concentration diminished the Cu and Cd binding capacity from 89 to 80% and 81.8–5.8%, respectively [66]. As such, the salt content of Sargassum must be monitored and maintained to support its function as biosorbent material. Table 2 shows the adsorption capacities of various *Sargassum* spp.

3.4. *Pharmaceuticals*

Sargassaceae are rich in phytochemicals which gives them unique therapeutic and medical properties [70,71]. Mehdinezhad et al. [72] reported that the high levels of the metabolites tannins, saponins, sterols and triterpenes in *S. angustifolium*, *S. oligocystum* and *S. boveanum* suppressed the growth of the cancerous MCF-7 cell line by $IC_{50} = 67.3$, 56.9, 60.4, respectively. These results support the application of these seaweeds in anti-tumor drug development.

The *Sargassum* genus also exhibits high polyphenolic content [70,72]. These bioactive compounds are important as they scavenge for cytotoxic free radicals, thereby enhancing the natural antioxidant potential [20,73]. Dichloromethane and ethyl acetate extracts of *S. wightii* display antihypertensive and antidiabetic properties in different vitro systems due to increased Fe^{2+} chelating activity [20]. Butanolic *S. wightii* extract contains steroids, flavonoids and sterols. When dosed at 100 mg/kg, Dar et al. [19] observed a 86.7% reduction in carrageenan-induced edema in rats. This inhibitory effect was superior to that of the traditional and non-steroidal drugs Aspirin and Ibuprofen, 79.4% and 57.3%, respectively [19]. Malini et al. [70] proved the potential of *S. longifolium* for anti-microbial and anti-inflammatory activities. Fourier-transform infrared spectroscopic analysis of the dimethyl sulfoxide extract revealed the formation of secondary metabolites which inhibited the growth of five different strains of bacteria and fungi [70].

Table 2
Heavy metal ion recovery by different *Sargassum* spp.

Biosorbent	Heavy metal source	Metal ions removed	Reference
Sargassum sp.	Aqueous solutions	Pb^{2+}, Cu^{2+}, Cd^{2+}	[65]
Sargassum sp.	Synthetic multi-metal solutions and urban storm water	Ni^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, Mn^{2+}	[64]
S. bevanom	Industrial wastewater	Cr^{6+}	[67]
S. natans	Industrial solutions	Au^{+}	[68]
S. fluitans, S. filipendula I, S. vulgare	Metal mining and processing materials	Cu^{2+}, Cd^{2+}	[18]
S. filipendula	Binary systems	Zn^{2+}, Cd^{2+}	[69]
S. sinicola	Saline wastewater	Cu^{2+}, Cd^{2+}	[66]

S. fusiforme has been studied for application in traditional Chinese medicine as a potential antiviral drug. Guo et al. [74] observed that *S. fusiforme* extracts diminished CD4 (HIV receptors) and T-cell HIV infection by 80% after 3 d, with more than 90% suppression achieved after 5 d. The high efficiency of *S. fusiforme* at preventing HIV replication supports its clinical testing in China and prospective utilisation in drug development [74]. Studies by Chen et al. [75] have also shown that *S. fusiforme* naturally lowers cholesterol levels. This reaction is triggered by the phytosterol constituents in *Sargassum* which promote cholesterol excretion in bile. Table 3 highlights the pharmaceutical properties of some *Sargassum* spp.

3.5. *Biogas*

Brown macroalgae are rich in water, carbohydrates and proteins but possess cell walls of low cellulose and negligible lignin content. This structural composition and nutritional content support microbial growth and degradation, thereby rendering these seaweeds viable

Table 3
Pharmaceutical potential of various *Sargassum* spp.

Species	Bioactive Properties	Cytotoxic Activity	Reference
S. angustifolium, S. oligocystum, S. boveanum	Anti-oxidant, anti-cancer	HT-29[a], HeLa[b] and MCF-7[c] human cell lines	[72]
S. wightii	Anti-inflammatory, anti-hypertensive	Cycloxygenase enzymes and inflammatory prostaglandins	[19,20]
S. longifolium	Anti-microbial	Bacterial and fungal pathogens	[70]
S. fusiforme	Anti-virus	CD4 and T-cell HIV infection	[74]
S. oligocystum	Anti-cancer, anti-tumor	Daudi (lymphoma) and K562 (leukaemia) human cell lines	[76]

Cancer cell lines:
[a] Colon.
[b] Cervical.
[c] Breast.

feedstock for biofuel production [77,78]. AD is a cost-effective and economically feasible bioconversion method. During this four stage biological process, micro-organisms degrade organic matter in an oxygen-depleted environment into biogas and a digestate. The AD process can be subdivided into the following phases: hydrolysis, acidogenesis, acetogenesis and methanogenesis [79]. Hydrolysis is the rate-limiting step of AD as it determines the bioconversion efficiency, volatile fatty acid (VFA) formation, fermentation process time and biochemical methane potential (BMP) [80].

Biogas is a renewable energy source composed primarily of methane (50–70%) and carbon-dioxide (30–50%). Trace elements and water vapour are also present in this gaseous fraction. While the high methane content of biogas is desirable, the presence of constituents such as carbon-dioxide, hydrogen sulfide and ammonia, reduce its calorific value. Upgrading biogas removes these impurities and yields bio-methane, an eco-friendly and energy-dense gas which can replace compressed natural gas for application in cooking, heating and electricity production. The digestate derived from AD is enriched with recycled nitrogen and phosphorus containing compounds and has fertiliser potential [78].

AD has been proven successful at converting a wide array of brown algal spp. into bio-methane [77,81]. Presently, sparse literature exists on the application of this bioconversion method to pelagic *Sargassum*. While no technological barriers exist to the use of this marine biomass in AD, the presence multiple recalcitrant components and seasonality of nutritional content must be considered and managed, for optimal methane productivity and to mitigate digester failure [77]. Presently, methanation of macroalgae achieves <50% of the theoretical methane potential (TMP) [82].

4. Challenges of *Sargassum* anaerobic digestion

4.1. Harvesting and seasonal variation

Sargassum blooms transport juvenile sea turtles, fish and entrap any plastic waste in their passage across the Atlantic Ocean into the neritic zone of Caribbean coastlines. When washed ashore, the marine biomass gathers sand, while hosting benthic organisms. Harvesting of *Sargassum* for AD therefore necessitates the successful removal of these particulates and as such, should not be done offshore. Sand and plastic waste effect fouling and increase technical issues in the digester while marine organisms should be removed and returned to their habitats [3]. Manual collection of shored *Sargassum* with rakes or by hand is simple and facilitates the careful separation of this marine biomass from aquatic life and unwanted pollutants. However, this process is very slow and tedious, incurring costs proportional to the size of the work-force employed [40,42]. Mechanical harvesting with cane loaders is a more efficient and effective. While the latter method increases the daily volume retrieved and diminishes the demand for a large work-force, a secondary facility is required to sort and clean the biomass prior to AD [83].

Further consideration must be given to the seasonality and unpredictability of *Sargassum* influx [83]. Inundation of the Caribbean region generally occurs between March and September annually. While satellite imaging technology has been deployed to monitor drifting *Sargassum* blooms [7,11], this biomass cannot be considered sustainable feedstock. *Sargassum* preservation techniques must be explored to ensure its continuous supply during intervals of scarcity [3]. Low-cost methods such as ensiling and sun-drying may be used to preserve seaweeds for yearlong supply to a digester, with minimal loss to the BMP [3,82].

4.2. Nutritional composition

Brown macroalgae contain 70–90% water [53] and 10–15% dry weight (dw) matter [84]. When dehydrated, carbohydrates dominate the composition, representing between 40 and 60% of the cell contents [85,86]. Proteins and lipids constituent 8–23% and 0.3–6% dw, respectively [3,87]. Bioenergy production from brown algae is dependent on the degradation of these nutritional components. However, microbial access to the proteins in these seaweeds is hindered by cellular localisation while the lipid fraction is very low and inconsequential on methane productivity [79]. Brown algae conversion to biofuels is therefore reliant on the degradation of its rich carbohydrate content. Nevertheless, the sugars in seaweeds are not readily available for digestion and vary with seasonality, thus lowering the BMP [3,16,85].

Alginate, the most abundant polysaccharide in brown macroalgae, peaks in quantity during summer months when ocean temperature and light irradiance are high. This property is an adaptation which supports cell vitality by preventing dehydration [88]. Laminarin and mannitol, products of photosynthesis exhibit maxima values during spring and summer, while fucoidans or sulfated sugars are prevalent in autumn [79]. Summer is therefore the preferred season to harvest brown macroalgae for optimum energy extraction [89].

In studies conducted by Adams et al. [88], the polysaccharide composition of *L. digitata* varied throughout the year with the lowest and highest yields recovered in March and July, respectively. Consequently, the methane productivity of this biomass improved from 196 mL/g of volatile solids (VS) in March to 254 mL/gVS in July. Similarly, Jard et al. [77] reported that the BMP of *S. latissima* harvested from May to August increased from 204 to 256 mL/gVS [77]. On the contrary, seasonality had little effect on the biomethanation of *S. muticum* with the low yields of 166–208 mL/gVS recovered from three different seasonal samples [90]. These findings suggest that while the polysaccharide content of *Sargassum* improves with seasonality, the biodigestibility of this fraction is restricted by the presence of recalcitrant components such as insoluble fibre [91].

4.3. Fibre

The absence of lignin in the cell walls of macroalgae facilitates the microbial breakdown of carbohydrates, proteins and lipids during AD. However, *Sargassum* spp. are enriched with insoluble fibre fractions which reduce the concentration of VS available to these microbes for decomposition [91,92]. Consequently, the genus exhibits a lower BMP, 120–190 mL/gVS, when compared to other species such as *Gracilaria* sp. (280–400 mL/gVS) [91], *P. palmata* (279 mL/gVS) and *S. latissimi* (204–256 mL/gVS) [77]. In a study comparing ten different macroalgal species, Jard et al. [77] reported that *S. muticum* contained 531 g/kg total solids (TS) of fibre. The presence of this rich insoluble fraction reduced the concentration of polysaccharides and proteins available for digestion and contributed to a BMP of 130 mL/gVS. This energy output was the lowest of the ten genera studied [77]. The low methanation of *S. muticum* was also documented by Milledge and Harvey [82] who recovered the maximum methane yield of 110 mL/gVS or 25% of the TMP.

4.4. Polyphenols

Sargassaceae are rich in polyphenols and therefore exhibit superior antioxidant and antimicrobial potential. However in AD, polyphenols poison and impair the function of methanogens, thereby effecting digester instability and mitigating methane generation [77]. García-Casal et al. [93] reported that *Sargassum* contains measured 80.39 GA E/g of polyphenolic content. These levels are significantly higher than the 10.84 and 18.43 GA E/g extracted from *Ulva* sp. and *Porphyra* sp., respectively. Jard et al. [77] suggest that the high polyphenols content of *S. muticum* (19.8 g/kgTS) contributed to the low BMP of this algae.

4.5. Sulfur

Brown seaweeds contain a higher concentration of sulfur than terrestrial energy crops [94]. While sulfates are necessary for methanogenic bacterial growth, elevated levels of these compounds promote salt accumulation and inhibit microbial digestion [95]. In a sulfur-rich medium, Marquez et al. [92] observed the growth of sulfur-reducing bacteria which compete with methanogens and lower the BMP. During fermentation, elemental sulfur is also converted to hydrogen sulfide. This corrosive gas increased bioreactor instability and reduced the quantity and quality of biogas generated from *U. lactuca* [96] but had no effect on the BMP of *S. muticum* [90]. Ensiling has shown promise at reducing the organic sulfur levels of biomass prior to AD [82].

4.6. Cations

The high metal ion content of *Sargassum* can lead to salt accumulation and reduced AD performance. Cationic elements such as Mg, Ca, Fe, Na, K and Al are not biodegradable and accumulate to toxic levels, consequently poisoning the microbial cultures and effecting reactor fouling [97]. The low K and Na cation levels of *P. palmata* and *S. latissima* promoted the digestion of VS and yielded 312 and 266 mL/gVS of methane, respectively. However, when the specific organic loading rate (OLR) and cation concentration were both increased, the methane productivity of these seaweeds diminished by approximately 50% [98]. Careful consideration should be given to this parameter for optimum biomethanation of *Sargassum* to be achieved [56].

4.7. Carbon to nitrogen ratio

Microbial growth and AD optimisation are dependent on a feedstock carbon to nitrogen (C:N) ratio ranging from 20–30:1 [99]. At C:N ratios below 20:1, carbon is quickly consumed resulting in VFA accumulation in the digester. The presence of excess nitrogen in the substrate also promotes ammonia formation and toxicity. In high concentrations, ammonia and VFAs poison methanogenic bacteria and reduce the substrate methane potential [100]. Studies by Marquez et al. [92] found that the C:N ratio of *Sargassum* spp. varies from 12 to 22, due to the rich elemental composition of 12–40% carbon and 0.6–2.0% nitrogen. *S. muticum* sampled from England and France exhibited C:N ratios of 8:1 [82] and 20:1 [77], respectively. Analysis of floating *Sargassum* blooms taken from the coast of Nigeria revealed a C:N ratio of 23:1 [16]. *S. tenerrimum* also displayed C:N ratio variation of 18:1 [99] and 23:1 [101] when collected from two different sites in India. Pelagic *Sargassum* has a C:N ratio of 47:1 in oceanic waters and 27:1 in neritic waters. The afore-mentioned deviations in the C:N ratio of *Sargassum* spp. are indicative of changes in the nutritional composition at each growth site and during the study sample season [10]. To amend the C:N ratio to 20–30:1 for optimum bioconversion efficiency and biogas output, co-digestion of *Sargassum* with another feedstock has been explored [99].

4.8. Salinity

Brown seaweeds contains approximately 15% dw of salt content due to its oceanic growth conditions [82]. This saline composition is greater than that of terrestrial plants and has a negative effect on methanogenesis [102]. At salt concentrations below 10 g/L, methanogenic bacterial growth is promoted. On the contrary, beyond the salinity of 10 g/L, an increase in osmotic pressure results in diminished microbial activity [94]. Zhang et al. [103] reported that at a salinity of 4.42 g/L, *Sargassum* sp. generated 501.85 mL/gVS of biogas enriched with 58.5% methane content. However, a rise in the salt concentration from 4.42 to 18.7 g/L reduces microbial activity by 10–90%, consequently reducing biogas and methane productivity by 223.91 mL/gVS and 168.26 mL/gVS, respectively.

The negative correlation between salinity and methane production was also observed by Yi et al. [104]. In this simulation study which utilized sea salt crystals to achieve the desired salt concentration, the authors measured optimum methane generation of 275.78 mL/gVS from marine macroalgae at a salinity of 15 g/L. Increasing the salt concentration from beyond this point to 85 g/L reduced the biogas yield and impeded the function of methanogens. Of note, the quantity of biogas and methane recovered at 35 g/L was identical to that achieved from the control sample (natural sea water) due to effective inoculum acclimatisation. This result suggests that seaweeds removed from the ocean can be applied directly as feedstock for AD [104]. Nevertheless, in instances where the feedstock salt content is excessive and detrimental to AD, it can be amended with ensiling [82].

5. Solutions to *Sargassum* anaerobic digestion

5.1. Pre-treatment

Pre-treatment technologies have been introduced prior to AD to enhance biomass hydrolytic cleavage and optimise the concentration of carbohydrates accessible for microbial digestion [78,105]. Methods including physical, thermal, chemical and biological pre-treatment have been applied to brown macroalgae to improve their BMP. Maceration accelerated the biomethanation of unwashed *U. lactuca* by reducing the particle size of biomass, thereby improving microbial access to organic matter for digestion [95,106]. Like *Sargassum*, the green seaweed *U. lactuca* has a C:N ratio below 20:1 and is enriched with sulfur, salt and insoluble dietary fibre. This chemical composition inhibits the growth of methanogenic bacteria and lowers the corresponding methane potential [95]. Bruhn et al. [106] reported that maceration promoted the degradation of fibrous components in *U. lactuca* and enhanced methane productivity by 56% [106]. This pre-treatment method also had a positive effect on the digestibility of *G. vermiculophylla* and *C. linum* but diminished the BMP of *S. latissima* relative to the untreated samples [95].

Laminaria sp. pre-treated in a Hollander beater for 10 min, generated 651 mL/gVS of biogas with 53% methane content. The biogas fraction collected from beaten seaweed samples was comparable to the yield predicted by Design-Expert v.8, a statistical software tool used to model reactor operating conditions for optimum biogas production [81]. Beating is more effective than ball milling and microwave pre-treatments. While the ball milling of *Laminaria* sp. to particle size 1–2 mm increased solubilisation, the process inhibited enzymatic hydrolysis and acidogenesis, consequently diminishing methane production by 21–27% relative to the raw seaweed. For optimum biomethanation to be achieved from ball milling, feedstock with minimal water content are necessary [107].

Microwave pre-treatment alters the structural composition of biomass by disrupting hydrogen bonds. This technology enhances the microbial hydrolysis of fermentable sugars but has a minor effect on solubilisation [108]. Montingelli et al. [107] reported that microwave irradiation had a negative effect on the bioconversion of *Laminaria* spp., decreasing the methane potential by 26%. From this result, the authors surmised that the conditions of microwave pre-treatment are too harsh for algae application but favour lignocellulose rich biomass. On the contrary, Vivekanand et al. [109] observed higher methane productivity from *S. latissima* pre-treated with steam explosion. Optimum methane recovery of 268 mL/gVS was achieved at 130 °C and represents an improvement of 20% relative to the raw sample.

Autoclaving *Sargassum* sp. at 121 °C for 15 min increased the soluble chemical oxygen demand (COD) by 10-fold. At the concentration ratio of 0.09 g/L inoculum and 2.5 g/L *Sargassum* sp. optimum methane recovery of 541 mL/gVS was achieved. This yield was 60% higher than the untreated sample. However, at higher Sargassum sp. concentrations, methane formation was suppressed by the accumulation of soluble inhibitory metabolites [110]. Washing and drying biomass prior to thermal pre-treatment reduces the concentration of recalcitrant compounds (salt and heavy metals) produced and improves the BMP [106].

Fungal pre-treatment has been proven to be more effective than enzymatic pre-treatment at improving seaweed biomethane production. Tapia-Tussell et al. [111] revealed that application of the fungi Bm-2 strain (*Trametes hirsuta*) enhanced lignocellulosic and hemicellulosic biodegradability in macroalgae consortia sampled from Mexico. After incubation for 29 d, the methane collected from this biological process was 104 mL/gVS or 28% higher than the untreated sample. Most importantly, fungal pre-treatment exhibited superior tolerance to the 35.5% ash, 19% phenolic and 78 g/L alkali metal content of this marine biomass. On the contrary, enzymatic pre-treatment achieved only 86 mL/gVS methane content. Table 4 highlights the effect of seaweed pre-treatment on methane productivity.

5.2. Co-digestion

The high C:N ratio of some brown macroalgal species such as *S. latissima* and *L. digitata* supports their mono-digestion for biogas production [113]. However, the low C:N ratio and high saline, phenol and cellulosic fibre content in species like *Sargassum* pose a challenge to AD, as these properties inhibit microbial degradation and mitigate biogas formation [91]. Moreover, the rich nitrogen fraction of this substrate promotes the formation of ammonia which causes digester instability and ensuing reactor failure [100]. To dilute the high salt concentration, lower the digester toxicity and augment the C:N nutrient balance for optimum biomethanation, seaweeds can be co-digested with other types of biomass [105].

Glycerol and waste frying oil improved the C:N ratio of *Sargassum*, enhancing substrate bioconversion to methane by 56 and 46%, respectively [114]. Yen and Brune [115] reported that the incorporation of 50% waste paper into algal sludge optimized the C:N ratio for co-digestion to 20–25:1. Moreover, paper increased cellulase activity in the digester and the concentration of nutrients necessary for the growth of methanogens. As such, a daily optimum methane yield of 1607 mL/L was recovered with a feedstock mix of 60% waste paper to 40% algal sludge at an OLR 5 gVS/L d. Latex serum [116] and wheat straw [109] are also good co-substrates for macroalgae.

On the contrary, sugar industry wastewater had a negative effect on biogas production from *U. rigida*. Co-digestion of these substrates at a ratio of 1:1 exhibited maximum biogas production of 114 mL/gVS, enriched with 76 mL/gVS of methane [117]. Dairy slurry also lowered the C:N ratio of *S. latissima* and *L. digitata* and promoted VFAs accumulation in the digester. For feasible continuous co-digestion of these substrates, Tabassum et al. [113] employed a feedstock mix of 2:1 seaweed to dairy slurry. Using this ratio, *L. digitata* and dairy slurry achieved a SMY of 232 mL/kgVS at OLR 5 kgVS/m^{3}d. At a lower OLR of 4 kgVS/m^{3}d, the SMY was 252 mL/kgVS [113]. These results oppose the work of Akunna and Hierholtzer [100] who observed increased reactor instability directly proportional to the concentration of *L. digitata* added to the feedstock. In this experimental setup, green peas were initially incubated for 15 d. Subsequently, seaweeds (2% dw) were introduced into the digester over a 15 d duration to replace green peas of equal weight and facilitate microbial acclimatisation. This change to the feedstock mix promoted the release of recalcitrant constituents and VFA accumulation in the reactor, thus diminishing methane productivity. Table 5 summarises the results of several co-digestion studies.

6. Case study: Barbados

6.1. Energy demand

Barbados is a 431 sq. km island nation located to the east of the Lesser Antilles island chain in the Caribbean Sea. This small island is a developing state of approximately 285,000 inhabitants (2016) and is heavily reliant on fossil fuel importation for energy production [118, 119]. These imports are predominated by heavy fuel oil and diesel [120], and account for 8% of the island's annual GDP. Between 1993 and 1999, imports of petroleum-based products represented 8.5% of Barbados' merchandise imports bill. However, the increased demand for fossil fuels in subsequent years necessitated increased budgetary allocations to 17% and 19% in 2005 and 2006, respectively [121]. This unsustainable practice has hindered the growth of the Barbadian economy, rendering it vulnerable to the high volatility of international oil prices. For example, in 2017, the Government of Barbados (GOB) estimated the cost of oil-derived products at Barbados dollar (BBD) $354 M, varying considerably from BBD $452 M and BBD $367 M in 2015 and 2016, respectively [118,119].

Table 4
Effect of pre-treatment technologies on macroalgal methane production.

Pre-treatment Method	Technique	Macroalage	Treatment conditions	CH_4 yield of the raw seaweed	CH_4 yield of treated sample	Effect on BMP (%)	References
Physical	Maceration	*U. lactuca*	Homogenized paste	174 mL/gVS	271 mL/gVS	+56	[106]
	Maceration	*U. lactuca*	Hand blended to homogenized paste	152 mL/gVS	255 mL/gVS	+68	[95]
		G. vermiculophylla		132 mL/gVS	147 mL/gVS	+11	
		C. linum		166 mL/gVS	195 mL/gVS	+18	
		S. latissima		340 mL/gVS	333 mL/gVS	- 2	
	Beating	*Laminaria* sp.	10 min	277 mL/gVS	425 mL/gVS	+53	[81]
	Beating	*Laminaria* sp.	10 min	328 NmL/gVS	335 NmL/gVS	+2	[107]
	Ball milling		18 h, biomass size (1 mm)		241 NmL/gVS	- 27	
	Ball milling		18 h, biomass size (2 mm)		260 NmL/gVS	- 21	
	Microwave		560 W, 110 °C, 30s	328 NmL/gVS	244 NmL/gVS	- 26	
Thermal	Autoclaving	*Sargassum* sp.	121 °C, 1 bar, 15 min	541 mL/gVS	339 mL/gVS	+60	[110]
	Hydrothermal	*U. lactuca*	110 °C, 20 min	174 mL/gVS	157 mL/gVS	- 10	[106]
			130 °C, 20 min		187 mL/gVS	+8	
	Steam explosion	*S. latissima*	130 °C, 10 min	223 mL/gVS	268 mL/gVS	+20	[109]
			160 °C, 10 min		260 mL/gVS	+17	
Thermochemical	Alkali	*P. palmata*	NaOH, 20/70 °C, 24 h	308 mL/gVS	365 mL/gVS	+19	[112]
			NaOH, 160 °C, 30 min		282 mL/gVS	- 8	
	Acid		HCl, 160 °C, 30 min		268 mL/gVS	- 13	
Biological	Fungal	Mexican Caribbean Macroalgae Consortiums	35 °C, 6 d	81 mL/gVS	104 mL/gVS	+28	[111]
	Enzymatic		40 °C, 24 h		86 mL/gVS	+6	

Table 5
Co-digestion of macroalgae and various substrates.

Macroalgae	Co-substrate	C:N ratio	CH_4 yield	Summary	References
Sargassum sp.	Glycerol/waste frying oil	–	157–283 mL/gCOD	• Mono-digestion of *Sargassum* sp. achieved 181 mL/gCOD, representing 52% of the TMP. • The high carbohydrate content of glycerol and waste frying oil optimized the C:N ratio and microbial fermentation of *Sargassum*, generating methane 283 mL/gCOD (56%) and 265 mL/gCOD (46%) methane when respectively co-digested.	[114]
S. latissimi	Wheat straw	21.6–81.6	214–270 mL/gVS	• *S. latissima* and Wheat straw have BMPs of 223 and 98 mL/gVS respectively. • A feedstock mixture of 75% macroalgae to 25% wheat straw exhibited optimum C:N ratio of 30.2, yielding 270 mL/gVS methane. • Inclusion of wheat straw into the substrate beyond this ratio effected C:N ratios exceeding 30:1 which inhibited methanogenesis.	[109]
U. rigida	Sugar industry wastewater	11.5	76 mL/gVS	• Continuous co-digestion of 1:1 decomposed *U. rigida* and diluted sugar industry wastewater in an anaerobic up-flow reactor for 75d produced maximum biogas yields of 114 mL/gVS with 67% methane.	[117]
Chaetomorpha sp./*U. intestinalis*	Latex serum waste (natural rubber)	15	196 mL/gVS	• Latex serum contains a rich VS fraction which facilitates the production of 398 mL/gVS biogas when digested. • Co-digestion of $\geq$50% latex serum with *Chaetomorpha* sp. and *U. intestinalis* produced 422–460 mL/gVS biogas with 25–42% methane.	[116]
S. latissima/L. digitata	Dairy slurry	15.70–23.40	232–252 mL/gVS	• Mono-digestion of *L. digitata and S. latissima* achieved a SMY of 330–338 mL/gVS, while dairy slurry achieved 138 mL/gVS. • When co-digested, dairy slurry reduced the C:N ratio of macroalgae and promoted VFA accumulation in the digester. • Feedstock ratio of 66:33 macroalgae to dairy slurry exhibited the highest methane yield. • Continuous co-digestion of dairy slurry with natural *L. digitata* achieved SMY of 232 mL/gVS at OLR 5 kgVS/m^{3}d. This was lower than the SMY of 252 mL/gVS effected by cultivated *S. latissima* and dairy slurry at OLR 4 kgVS/m^{3}d.	[113]
L. digitate	Green peas	–	275–375 mL/gVS	• Green pea mono-digestion produced 5500 mL/d of methane at OLR of 2.67 kgVS/m^{3}d. Substitution of 2% green peas with *L. digitata* promoted VFAs formation which inhibited methanogenesis and rendered the digester instable. Removal of the seaweed from the feedstock restored digester functionality. • At lower OLR (0.77 kgVS/m^{3}d), microbe activity and reactor stability improved, supporting the incorporation of 2–10% seaweed into the feedstock. Reactor stability was also established at OLR 1.25 kgVS/m^{3}d and feedstock ratio of 35% seaweed, generating 500 mL/gVS biogas of 55–65% methane content.	[100]
U. lactuca	Cattle manure	–	206–259 mL/gVS	• The total methane yield of cattle manure reduced inversely proportionally to the concentration of dried *U. lactuca* added to the feedstock. Optimum total methane yield of 259 mL/gVS was realised at feedstock ratio of 80% manure to 20% macroalgae. • On the contrary, incorporation of 40% *U. lactuca* into the substrate boosted the weight SMY by 48%.	[95]

6.2. Electricity production

The primary electricity generator/supplier in Barbados is the Barbados Light and Power Company (BLPC). This privately-owned utility company controls the operation of three oil and diesel power stations island-wide with a combined installed capacity of 239.1 MW and a small-scale 10 MW solar photovoltaic farm. A modest volume of natural gas is produced onshore but its consumption is limited to cooking [118,119].

Annually, electricity generation in Barbados increases by 1.2% in line with the growing domestic sector which consumes approximately 33% of the supply [121]. Analysis of electricity sales between 2015 and 2016 reflect an expanding energy demand, from 933 to 944 GWh, respectively [122]. However, the sale price of electricity derived from fossil fuels is not fixed and fluctuates with global oil costs [123,124]. Fossil fuel combustion for electricity generation is 37% efficient [120] and incurs heat and waste losses of 40% during production, distribution and transmission [122]. This process is also unsustainable and environmentally harmful, emitting 837,000 tonnes of carbon-dioxide in 2009 [121].

In an attempt to reduce energy costs, improve energy security and maintain environmental integrity, the GOB has developed a National Sustainable Energy Policy. This framework sets the target of 29% green electricity generation by 2029 [125] and the replacement of 75% imported heavy fossil fuels with renewable energy sources by 2037 [120]. This transition would diversify the national energy matrix and mitigate the island's carbon footprint [121]. Annually, Barbados could achieve energy savings of approximately BBD $720 M and reduce its total expenditure by BBD $2.2 B [120].

6.3. Waste recovery

Solid waste management in Barbados is the shared responsibility of four government agencies, led by the Ministry of Health. Of the four agencies, the Sanitation Service Authority holds the primary mandate of waste collection, treatment and disposal [126]. During the first quarter of 2015, Barbados generated approximately 26 kilotonnes of waste per month [126]. This represented the daily production of approximately 1000 tonnes of waste and a fivefold increase, when compared to the daily recovery of 200 tonnes of waste in 1994 [127]. According to the World Bank, in 2012, Barbados collected 4.75 kg/capita/d of urban organic municipal solid waste (OMSW), almost double and triple that of the United States (2.58 kg/capita/d) and United Kingdom (1.79 kg/capita/d), respectively [128]. The steady increase in per-capita waste in Barbados reflects a growing, developing and industrialized population [121,126].

The Mangrove Pond Landfill is the main waste disposal site in Barbados. This facility houses the Sustainable Barbados Recycling Centre (SBRC) where incoming waste streams are sorted to salvage organic and recyclable materials, thereby mitigating landfill waste disposal by 70% [121]. Barbados' waste stream is dominated by organic material as shown in Fig. 1. At the SBRC, 150 tonnes of green waste is collected daily for composting. Recyclables such as metals, plastics, paper, e-waste and batteries are exported to foreign markets, given their high commercial value [126]. Hazardous chemical waste from hospitals and chemical laboratories are shipped to Canada for disposal. Glass, construction and demolition (C&D) materials are landfilled [121].

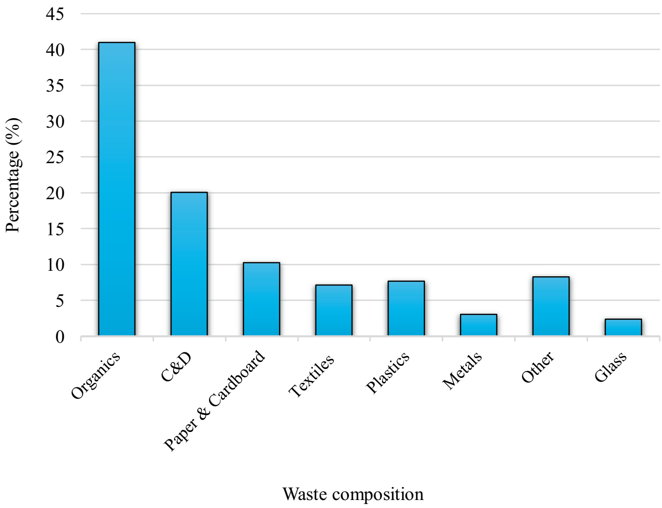

Fig. 1. The composition of Barbados' 2015 waste stream.
Source: PMCU [126].

6.4. *Anaerobic digestion of Sargassum*

In the absence of holopelagic *Sargassum* for chemical analysis, this work will rely on the chemical composition available in literature. According to the single study conducted by the CPI [22], *Sargassum* sampled from the Caribbean island of St. Lucia generated biomethane with an energy value of 11.77 MJ/kg and electricity potential of 2 MWh per tonne of biomass [22]. Estimating *Sargassum* influx into Barbados as 10,000 tonnes per annum based on the statistics from the 2015 inundation event [1], the mono-digestion of this biomass would potentially yield 20 GWh/yr or 2.11% of the 944 GWh of electrical power demanded in 2016.

Alternatively, the co-digestion of *Sargassum* with OMSW is more feasible and should be explored. In 2015, Barbados generated 361 kilotonnes of waste [129], 41% of which was organic (Fig. 1). This waste stream is sustainable and increases in volume annually in direct proportion to the population growth. As such, OMSW can be consumed as the primary substrate for AD and *Sargassum* incorporated into the feedstock mix during periods of massive beaching. Assuming the composition of the 2015 organic waste stream collected to be 100% food waste (FW) with an energy output of 0.618 MWh per tonne [22], its mono-digestion could achieve 91.35 GWh electricity. Bio-energy production could potentially be enhanced to 111.35 GWh by the co-digestion of *Sargassum* and FW, thereby satisfying 11.80% of the country's 2016 energy demand. Moreover, paper waste can be repurposed from exportation and integrated into the AD feedstock, increasing the energy output to 112.44 GWh.

These findings provide meaningful insight into the energy that can be derived from the co-digestion of the organic substrates in a bio-digester, functioning at optimum (100%) process efficiency. However, the figures presented are an optimistic scenario, based on the assumption of complete feedstock degradation and maximum substrate biomethanation. As such, the theoretical yield is an ambitious estimation of the actual gas yield that can be obtained.

Noteworthy, prior to the utilisation of biogas for energy generation, the H_2S content must be assessed given the rich sulfur content of brown macroalgae. In high concentrations, H_2S is highly toxic and corrosive to pipelines and machinery. Moreover, H_2S diminishes biogas quality and prohibits consumption in co-generation engines as its combustion promotes the production of sulfur dioxide. The maximum acceptable H_2S level for cogeneration engines is 150 mg/m^3 or 100 ppm. Treatment of unprocessed *Sargassum* seaweeds and the biogas recovered from AD are suggested to reduce H_2S production and toxicity [96].

6.5. *Fertiliser production*

In addition to biogas, AD produces a nutrient-dense solid-liquid digestate with fertiliser properties. Prior to use, the solid-liquid interfaces must be separated, consuming approximately 20% of the total energy generated from AD [130–132]. The solid fraction recovered can be applied directly in agriculture. Conversely, the high ammonia content of the liquid fraction impairs its utilisation and warrants reduction via one of four treatment methods: ammonia stripping, evaporation, reverse osmosis and struvite precipitation [133]. Liquid digestate treatment demands up to 10% additional energy and is therefore only economically viable when converting feedstock of high energy value [130,134].

The heavy metals in seaweeds also remain in the digestate after AD, contaminating and restricting its use as an organic soil conditioner. These cations accumulate in agricultural soils with repeated fertiliser application, inducing soil acidification and toxicity which stunts plant growth and diminishes crop productivity. Moreover, heavy metals are hazardous to human health and ecosystems through direct ingestion and physical contact. To capture heavy metal contaminants and mitigate the associated risk of soil poisoning, remediation techniques such as soil washing, phytoremediation and immobilisation can be incorporated. Presently, the aforementioned technologies are inexpensive, eco-friendly and exist globally in several developed countries [135,136].

Barbados has a rich agricultural heritage, founded on the production of sugar for supply to foreign markets. However, over the last decade, food and sugar production has drastically declined rendering the island food-scarce and dependent on i.mportation. Local application of AD fertiliser products would revive and support food and sugar production, thereby reducing expenditure on food imports. Moreover, potential is created for Barbados to generate capital and boost economic growth through the exportation of bio-fertiliser products, given the global shift away from chemical fertilisers to eco-friendly organic fertilisers.

6.6. *Implementation and industrial scale-up*

AD refineries have been commissioned worldwide for the conversion of biogenic waste streams such as sewage sludge, FW and lignocellulosic biomass into energy. To date, seaweeds have not been commercially introduced as feedstock for this treatment process. While the utilisation of macroalgae in AD is advancing, further research is required to address the challenges of high transport cost and seasonality. Large-scale seaweed cultivation has been explored in the US, Japan and across Europe as a method of providing a steady-state supply of this biomass for digestion. However, this process is costly and demands a 75% reduction in the current cost of the raw material for viable implementation [94]. Ensiling has also been proven effective at preserving seaweeds for up to 90 d for biofuel production downstream. Optimisation of this process is therefore necessary to support the development of a viable seaweed biofuel industry [137].

AD plants are less expensive than thermal waste treatment technologies and can be easily scaled-up to meet the energy demand. The capital cost to deploy a large centralised digester of 30,000 tonnes per annum is estimated at US $4 M [22], approximately one-tenth of the value of an incineration plant of equal capacity [138]. While the operation and maintenance costs of running an AD facility are low, a waste sorting facility is required to aid bioconversion [22]. Presently, there is a facility in Barbados, the SBRC [121]. The incorporation of a digestate treatment facility would enhance the process profitability but contribute to higher investment and operational costs [134]. Returns on the financial investment for a large scale plant can be achieved within five years of operation [22]. The lifespan of a well-maintained digester is approximately 20 years [134].

7. Conclusions and policy implications

Sargassum inundation of Caribbean beaches has reached crisis proportion, negatively impacting the fisheries, tourism and ultimately, financial sectors. It is paramount that this issue be addressed to restore the region's coastal beauty, viability and competitiveness. While many studies have explored the valorisation on brown macroalgae, literature on the biomethanation of pelagic *Sargassum* is sparse. This work therefore investigated the economic feasibility of utilising these seaweeds for biogas and fertiliser production in Barbados.

The results of this study suggest major benefits to Barbados' economy in general, and its renewable energy sector, in particular. The removal of *Sargassum* from the island's beaches for bioenergy production would restore the natural coastal aesthetics and contribute to economic growth in both the tourism and fisheries sectors. However, *Sargassum* spp. are poor feedstock for mono-digestion and sustainable energy production given their unpredictable influx volume and low methane productivity. Seaweed and organic waste co-digestion is more advantageous, yielding biomethane with the potential of supplying 11.80% of the electricity demand in 2016. This gaseous fraction also has application in cooking as a substitute for fossil fuel-derived natural gas. The energy generated from AD would mitigate the GOB's expenditure on imported petroleum-based products and better advance the island to its target of 29% electricity generation from renewable energy sources by the year 2029 [125]. The daily generation of large volumes of organic waste is an asset which would sustain the AD process in the absence of seaweed inundation events. Utilisation of this waste stream in AD would reduce the demand for its landfill disposal, thereby diminishing greenhouse gas emissions and solidifying the country's commitment to combat climate change as agreed through the ratification of the Paris Agreement [139]. Additionally, the complimentary bio-fertiliser generated from AD would support the local agricultural sector and improve food security. There is also potential for Barbados to gain revenue from the supply of organic fertiliser products internationally.

While Barbados' land mass is small, its socio-economic and energy profiles are representative of other islands in the Caribbean community. As such, the opportunities derived from the co-digestion of *Sargassum* and OMSW in Barbados could also be achieved in other small island nations region-wide. Moreover, there is potential for seaweed energy extraction further afield in larger territories such as Mexico, Florida and West Africa where *Sargassum* inundation has become problematic.

Presently, AD technology is not exploited in the Caribbean. For the commercialisation of this waste-to-energy process to be realised at all scales region-wide, government and stakeholder approval, coupled with the removal of all financial and political barriers, are necessary. Energy policies must also be developed to create a climate conducive to investment by, and partnerships with, the private sector and international agencies. Public education and engagement campaigns involving the use of social media and commercial marketing strategies would be required to promote AD reliability and efficiency.

Prior to the utilisation of pelagic *Sargassum* as feedstock for AD, a deeper understanding of this marine biomass is necessary. Future research on *Sargassum* blooms should investigate the seasonal fluctuations in the chemical composition and seek to develop early warning systems which can predict and quantify inundation events. Preservation techniques are also necessary to ensure the continuous supply of seaweeds for fermentation. The success of a seaweed biofuel industry depends on the energy balance and as such, a comprehensive techno-economic assessment must be conducted to evaluate the feasibility of implementation and commercialisation.

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