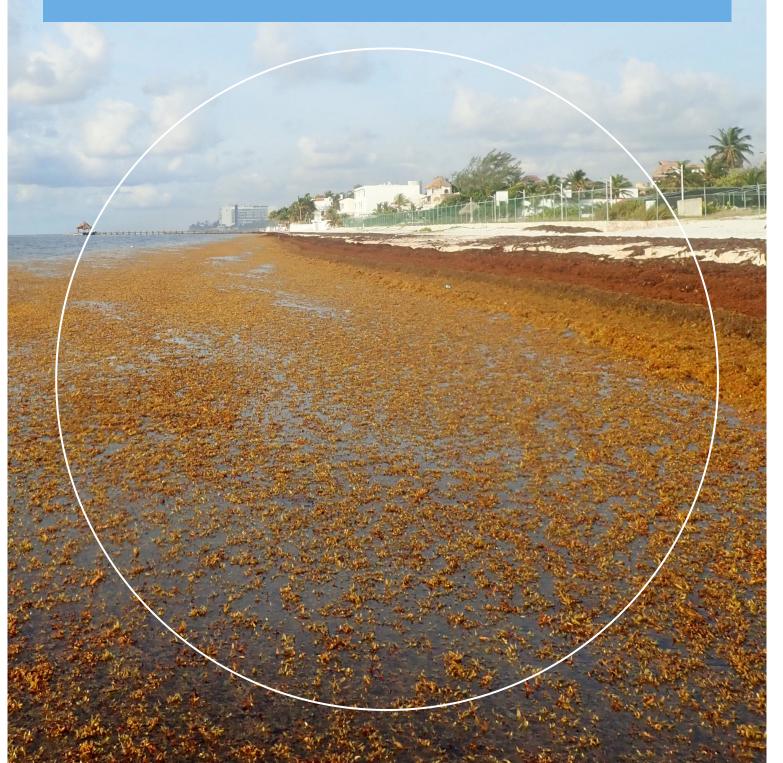
# Sargassum in Mexico: From environmental problem to valuable resource

A.M. López-Contreras, P. Núñez Valenzuela, B. Celis García, J. Driegen, E. Huerta Lwanga,P. Domin, M. Polett Gurrola, R. Rosas-Luis, Y. Verde Gómez, T. de Vrije

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Institute: Wageningen Food & Biobased Research

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Cover photo: Beach by Puerto Morelos with Sargassum, photo credit: B. van Tussenbroek

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### Summary

In recent years, large amounts of floating species of *Sargassum* seaweeds have arrived on the coasts and beaches of some Caribbean islands, the Gulf of Mexico, Northern Brazil, and West Africa. These beaching events appear to be recurring almost every year and cause major environmental, health, and economic problems in the affected areas. These *Sargassum* influxes threaten the already fragile coastal ecosystems, such as coral reefs, mangroves, and seagrass beds; they also disrupt the livelihoods of communities, especially those associated with the tourism and fishing sectors. This study aimed to develop strategies for valorization of the sargassum biomass that arrives to the coasts of the Gulf of Mexico. The present study is the result of the project "ValoSarg", financed by the Dutch program Kansen voor Morgen in 2021. This project was carried out as a collaboration between Mexican researchers at IPICYT, Wageningen University and Research and the company AllOptimal b.v. The project was coordinated by Wageningen University and Research under the supervision of the Agriculture advisor of the Dutch Embassy in Mexico.

This report includes a compilation of data on sargassum origin, composition, policies, management, and uses from a variety of resources, with a focus on the Mexican situation. We have consulted scientific literature, (governmental) public reports, internet resources; and discussed with parties involved in sargassum research or use, in order to formulate strategies for building new value chains for valorization of sargassum biomass. Besides the fundamental research by Universities or Research Centers on many sargassum-related topics, such as biology, biorefinery or applications, in Mexico, several commercial activities relate to sargassum harvesting, valorization and innovations. Most of these activities are being developed by small companies and entrepreneurs, and they are still not implemented on a larger scale. At universities and research centers there are activities on innovations and on fundamental research around sargassum.

The different steps of such a value chain include sourcing of feedstocks (Sargassum, organic wastes), logistics and storage, processing of biomasses to products, product evaluation, markets, social and techno-economic impacts, and overall sustainability (Fig. 1). For each area, the value chains need to be adapted taking into account the local conditions, such as the socio-economic situations, logistics, markets for the feedstocks and products, current uses of the feedstocks, environmental impacts or the development of the industry at the local level.

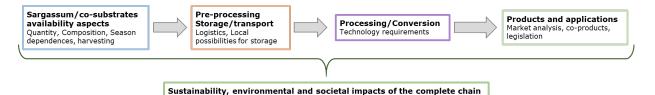


Figure 1 Generic scheme of a value chain using sargassum biomass as co-feedstock

The state-of-the-art of harvesting and storage technologies has been reviewed, and examples of these technologies currently applied in Mexico or elsewhere are described (section 2). Because of the negative environmental impacts associated with the beaching events, it is preferable to prevent them and harvest the biomass just before it reaches the coast. Also, in this way, the biomass could be kept free of sand, making possible the subsequent storage and conversion of the material.

In addition, experimental tests were carried out on the use of sargassum biomass for two applications considered to have the potential to be valuable in the Mexican situation:

1. Production of biogas at laboratory scale by anaerobic digestion of the sargassum biomass as such or in combination with food waste (Section 3). From the results obtained during this project at IPCYT, we can conclude that sargassum biomass can be kept stable during long periods using ensiling types of storage. This study also shows the effective use of a thermochemical pretreatment to improve the methane production from a two-year ensiled sargassum sample harvested in Cancún, and the successful co-digestion of pretreated sargassum with food waste. The relatively high biochemical methane production (BMP) values achieved in the present investigation (780.76 ± 34.44 mLCH4/gVS) when using a combination of 50% pretreated sargassum and 50% of food waste, show the potential of this approach. Considerations to be taken into account for upscaling this process using sargassum as a (co)feed have been described by All Optimal b.v. (Section 4). This company has extensive experience in commercial anaerobic digestion plants and processing of organic wastes for applications in agriculture, including sargassum biomass.

2. Preliminary tests on the use of sargassum biomass as substrate for vermicomposting (Section 5). The results of these tests show that worms could grow on sargassum mixed with old paper. Further research is needed to characterize this application.

To select the technologies for valorizing or marketing of the products, implications related to the chemical composition of the sargassum biomass need to be taken into account. In general, sargassum biomass is rich in salt, heavy metals, and/or (inorganic) arsenic, with concentration levels that could be higher than those permitted for crops or biomasses to be used in the food chain. Therefore, applications of sargassum or fractions of sargassum in the food chain need to be very well characterized. Some uses for sargassum streams, outside agriculture and the food chain, have also already been defined.

Multiple uses of the sargassum biomass, in some cases using biorefinery approaches, are being developed in Mexico and implemented by local enterprises. Section 6, provides an overview about the current most relevant applications. The most advanced toward commercialization are several initiatives to produce different types of materials for construction, and polymers for applications in textiles, for example. The content in salts and metals in sargassum biomasses opens the opportunity to use it as component/feedstock for nanostructured tailored materials for multiple applications. Examples are nanocarbons to be used in electrodes or in materials where antibacterial activity is needed. These applications are still under development at a laboratory scale.

In section 7, policy challenges and advice regarding the management of *Sargassum* influxes, in general, are described. In Mexico many activities relate to sargassum harvesting, valorization, and innovations. Most of these activities are developed by small companies and entrepreneurs, and they are still not implemented on a larger scale. At universities and research centers, there are activities on innovations and fundamental research. In recent years, knowledge of the management of sargassum biomass and mitigation plans to minimize impacts have been developed. However, this knowledge needs to be further translated into standard protocols and implemented in the affected areas.

Section 8 describes the plans for following up the research lines, including information on stakeholders. The main conclusions of this section relate to launching programs for stable financial and entrepreneurship support to local parties that are creating new value chains. These programs, which need to be easily accessible and have a continuation in time, will contribute to building the right environment for the implementation and long-term viability of the new value chains related to the sargassum uses. Where possible, integration of the new chains with existing chains or processes would be favorable.

Since the sargassum blooms need a multidisciplinary approach to be managed successfully, a collaboration between local, regional, and international stakeholders is necessary. National research programs exist already in several countries, including Mexico. Expansion of the international cooperation needs to be supported, using the tools available, and implementing new ones, where stakeholders from different areas can get funding for innovation and knowledge exchange.

# 1 The Brown Tide biorefinery: Valorization of the Sargassum biomass

#### 1.1 Sargassum and the Sargasso Sea

The genus *Sargassum* belongs to the class *Phaeophyceae* (brown algae), order *Fucales*, and family *Sargassaceae*. Approximately, 265 genera and 2040 species have been described within the brown algae, which comprises complex multicellular organisms; most of the species (95%) are widespread in cold to temperate waters [1]. As macroscopic organisms, brown algae possess key features that enable them to thrive in harsh environments, such as cell to cell communication and adhesion, tissue differentiation, and the ability to grow three-dimensionally [2]. The order *Fucales* comprises more than 500 species and nine families; members of this order and *Laminariales* are of ecological and economical importance. The family *Sargassaceae* comprises about 30 genera [2]. Generally, members of the brown algae are less prevalent in tropical regions, but the genus *Sargassum* has managed to occupy large habitats, similar to those of kelp, in the oligotrophic and warm tropical waters. Currently, the genus *Sargassum* comprises 350 recognized species mostly distributed in the subtropical and temperate regions of the world [2]. More than 60 species of benthic *Sargassum* inhabit the Atlantic ocean, while *S. fluitants* and *S. natans* (hereafter sargassum) are the most common pelagic species [3]. These two species are the dominant macroalgae of the Sargasso Sea, which comprises 99% of the total sargassum biomass [4,5].

The Sargasso Sea is a body of water within the northern Atlantic Ocean (approximately 20°-40° N to 30°-75° W) located in the center of the North Atlantic Gyre, which concentrates huge mats of sargassum floating freely due to the buoyancy provided by little spherical structures known as air blades or pneumatocysts [6,7]. The floating feature of sargassum enables a unique ecosystem; down to the open sea, the entangled floating mass act as floating islands that provide shelter, substrate, and feeding and spawning grounds for a diverse congregation of fishes, invertebrates, sea turtles, pelagic birds, and marine mammals. It also serves as a nursery for a great variety of endemic or vulnerable creatures [5,8,9]. There are over 100 species of fishes and 145 species of invertebrates associated with the habitats created by sargassum, with at least ten endemic species such as the sargassum shrimp (*Latreutes fucorum*) and the sargassum fish (*Histrio histrio*) [10].

The economic potential of the Sargasso Sea, as a provider of commercially important fish (e.gr. mahi-mahi, amberjacks) and other goods and services, has been estimated to be from over US\$ 200 million (fisheries) to US\$2.7 billion (all services) [11]. Besides its function as a habitat, the Sargasso Sea has some of the highest primary productivity in the world, representing a key area for carbon sequestration into the ocean and is recognized as "the golden floating rainforest of the Atlantic Ocean" [10]. Interestingly, in 2011, the net sink of carbon dioxide in the Sargasso Sea represented nearly 7% of the global carbon pump [12]. Recent studies revealed that the abundance and density of sargassum in the Sargasso Sea varies greatly with space and time [6,13].

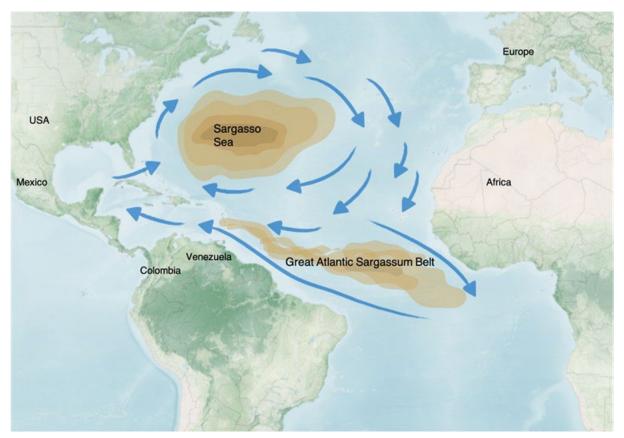
#### 1.1.1 Where do golden tides come from?

Since 2011, large amounts of pelagic *Sargassum* blooms have suddenly arrived to the coastlines of the Caribbean and tropical West Africa [3,13]. The term "Golden tides" refers to the accumulation of brown macroalgae from the genus *Sargassum* nearshore coastal waters of the north hemisphere, the tides usually occur during spring to summer [14,15]. Other terms used to refer to the golden tides are: sargassum arrival, bloom, influx, or inundation; massive influx or arrival; sargassum events; macroalgae blooms, among others.

Massive golden tides have been observed from the Coasts of China and Korea to the Eastern Pacific Coast, West Africa, the Brazilian Amazon coast, the Caribbean, and the Gulf of Mexico. Once in the coast, the golden tides may cause several ecological and environmental problems to marine ecosystems, which in turn have economical and societal impacts.

Concerning the sudden massive influxes of sargassum to the coasts of the Caribbean reported in the summer of 2011, recent studies highlight that the blooms originated due to a "tipping point" in climate in 2010 [3]. In

Winter 2009-2010, extreme winds and surface currents caused *Sargassum* to drift from the Sargasso Sea (western subtropics) towards the eastern Atlantic (offshore of Gibraltar, Spring 2010). For one year, the North Equatorial and Canary currents advected *Sargassum* southwest and southward, spreading it into the Caribbean and Tropical Atlantic [3], as shown in Figure 2.



*Figure 2* Simplified map showing the location of the Sargassum Sea and the Great Atlantic Sargassum Belt

Since then, sargassum has been recirculating in the so-called Great Atlantic Sargasso Belt, where it flourishes fueled by seasonal regimes of light, temperature, and nutrient availability promoted by eddy diffusion and mixing on the surface. A new regime was then established, the Great Atlantic Sargassum Belt has been formed in the summer months of almost every year since 2011 and each spring-summer, *Sargassum* is advected to the Caribbean and Gulf of Mexico [3]. In 2018, the Great Atlantic Sargassum Belt extended 8850 km long from the coasts of West Africa to the Gulf of Mexico and was estimated to contain around 20 million tons of *Sargassum* [16]. The outflows of the Mississippi, Amazon, Orinoco, and Congo rivers, and the upwelling plumes in the eastern Atlantic have been pointed out as the main contributors of nitrogen and phosphorus [3, 16–18], supporting the formation of the Great Atlantic Sargassum Belt. In addition, other factors that affect seawater environmental conditions (temperature, light irradiance, salinity), such as climate change, may be responsible for the warmer surface waters and the increased runoff of nutrients to the sea.

With enough nutrients and the right temperature, pelagic *Sargassum* is self-sustained because it reproduces by vegetative fragmentation, algae undergo rapid growth and break into smaller pieces; winds, waves, and boats also contribute to mechanical fragmentation. The offshoots will form mature plants completing the reproductive cycle [19]. *Sargassum fluitans* and *Sargassum natans* are the only two recognized species of pelagic *Sargassum*; these species are unique among floating macroalgae because their entire life cycle is afloat. Both *Sargassum* species are identified by blades, a highly branched thallus, and air bladders, which provide buoyancy and support the floating habitat in the ocean (Fig. 3). After a close look, three morphotypes have been identified in the massive influxes of *Sargassum* to the coasts, *S. fluitans III* and *S. natans I* dominating in the Sargasso Sea, and a rare morphotype of *S. natans* (*S. natans VIII*), which predominates in the tropical Atlantic [18–21]. The main differences between the three morphotypes are found in the shape of the leaves, axes, and air bladders.

Globally, the unprecedented large quantities of macroalgae and recurring algal blooms observed in the Atlantic (Northern Brazil, Greater Caribbean, Gulf of Mexico) and the Pacific coasts (East China and Korea) could be considered as ecological indicators of oceanic eutrophication [14,17].

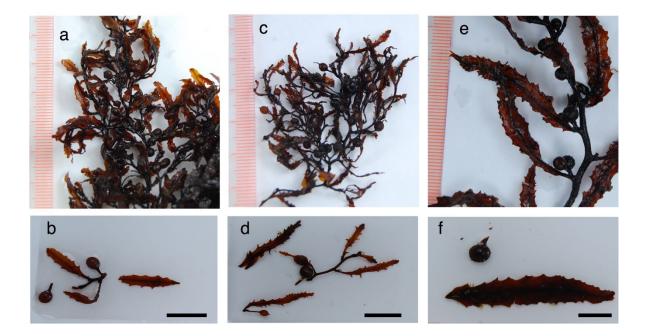


Figure 3 Morphology of the sargassum species found at the beach in Puerto Morelos, Mexican Caribbean. (a-b) S. fluitans III, (c-d) S. natans I, (e-f) S. natans VIII. The orange scale (a, c, and e) is in centimeters. The black bar (b, d, and f) is 1 cm

#### 1.2 Sargassum blooms in the Caribbean and their impacts

In the northern section of the Mexican Caribbean, the golden tides started arriving between 2014 -2015, with a critical peak achieved in May 2018 when approximately 8793 m<sup>3</sup> km<sup>-1</sup> of biomass were removed from the coast between Cancun and Puerto Morelos [22]. The first observations of massive arrivals of sargassum in the Eastern Caribbean and the African west coasts started back in 2011-2012 [13] and since 2011, sargassum has arrived on the coast of the Caribbean territories of all the 25 members of the Association of Caribbean States (Antigua and Barbuda, The Bahamas, Barbados, Belize, Colombia, Costa Rica, Cuba, Dominica, Dominican Republic, El Salvador, Grenada, Guatemala, Guyana, Haiti, Honduras, Mexico, Jamaica, Nicaragua, Panama, St. Kitts & Nevis, St. Lucia, St. Vincent & The Grenadines, Suriname, Trinidad & Tobago and Venezuela) and its eight Associate Members (Aruba, Curacao, France (on behalf of French Guiana, St. Barthelemy, and St. Martin), Guadeloupe, Martinique, Sint Maarten, The Netherlands (on behalf of Bonaire, Saba, and Sint Eustatius), and Turks and Caicos) [23].

The impacts of massive influxes of *Sargassum* to the coasts are detrimental to the entire coastal ecosystem affecting the goods and services that human communities depend on. Once pelagic sargassum reaches the coast, most of the biomass will remain onshore, causing a series of detrimental impacts (Fig. 4).



Figure 4 A) A golden tide arriving to the coast; B) Close-up of the brown tide; C) Collection of beached Sargassum with heavy machinery. All photos are from a beach in Puerto Morelos, Quintana Roo, Mexico; taken in August 2019. Photos by B. Celis

At the ecosystem level, sargassum blooms endanger coastal ecosystems causing an unbalance of the native benthic communities and affecting the biodiversity and trophic chains [4,9,24,25]. Recently, Martin et al. [19] found that the epifaunal assemblages on the different morphotypes of pelagic Sargassum (i.e., S. natans VIII, S. natans I, and S. fluitans III) seemed to vary according to the morphological complexity. Snails and flatworms were associated preferably with S. natans VIII and S. fluitans III, which provide a higher surface area for attachment, than S. natans I. At the trophic level, S. fluitans III harbored a more tropically diverse community because it attracts and concentrates prey species. The authors also proposed that co-occurrence of the new common morphotype S. natans VIII could alter the available trophic resources and endanger the already threatened or commercially important species. The nearshore floating sargassum causes changes in the benthic community structure and function, with the coral reefs and seagrass nursery habitats being the most impacted. Under sargassum mats, dissolved oxygen can reach anoxic levels (0.5 mg/L) and light incidence can reduce by 73%, while temperature could be 5°C warmer; all these changes impacted negatively (seven-fold decrease) the primary productivity of the seagrass Thalassia testidium [26]. Seagrasses protect the coasts from erosion and provide nurseries for fish, enhancing biodiversity. Shortly after its arrival on the beach, sargassum begins to rot, and the color of the algae changes from light brown-golden yellow to dark brown, causing sargassum brown tides [9]. The leachates of these enormous decomposing amounts of biomass cause an increment in water turbidity, depletion of dissolved oxygen (hypoxia or anoxia), decrease of pH in the seawater, increases in the concentrations of N and P; overall causing the mortality of seagrasses, coral reefs, and their associated fauna, and eventually the eutrophication of coastal waters [9,24]. Reversing the losses of the seagrass meadows and coral reefs may take decades [9]. Leachates from the decomposing sargassum biomass also affected the larval swimming behavior of the coral Acropora palmata, reducing its larval dispersal and genetic diversity [27]. This coral was once a keystone and structural species in the formation of Caribbean coral reefs, but since 2008 is a threatened species [28].

At the faunal level, the piles of sargassum accumulated on the beach can modify the nesting behavior of turtles at best or impede turtles from nesting beach areas at worst. After egg-laying, the brown tide can

create lethal temperatures for the developing embryos. If successfully hatched, the baby turtles may have difficulties reaching the ocean; other commercially and ecologically important species such as land crabs (*Cardisoma ghuanumi*) may also experience difficulties in releasing their eggs into the ocean [29]. In 2018, faunal mass mortality in the Mexican Caribbean was observed due to hypoxia and inadequate water quality due to sargassum decaying biomass after a brown tide event and the majority of the affected species were fish and crustacea [22].

At economic and social levels, the massive sargassum influxes also harm two of the major economic sectors of the entire Caribbean region: Tourism and fisheries. The tourism industry, on which the many Caribbean States depend, has been the most impacted and has experienced an income decrease because of the massive amount of sargassum at the shore [30]. The major attraction of the Caribbean beaches, with white sand and crystal-clear turquoise-blue waters, no longer exists after a sargassum event (Fig. 4) and deters tourists from going on vacation to the Caribbean. As an example, tourism in Solidaridad (near Tulum), Quintana Roo, Mexico, dropped by 35% during the first quarter of 2018 due to sargassum inundations [31]; the tourism trade in Quintana Roo state was valued at about US\$15 billion annually before SARS-CoV-2 pandemics [32]. Also, hotels spend money to clean up beaches and transport the sargassum biomass to disposal sites. Specialized boats that collect sargassum offshore can cost up to US\$1 million, and barrier lines could cost around US\$300 per linear meter [33]. For instance, in the late summer of 2019, the Mexican government spent US\$17 million on seaweed removal efforts [34]. The Mexican navy has attempted to stop the golden tides before reaching Cancun and Riviera Maya beaches, harvesting sargassum from the barriers offshore. In May 2021, they collected more than 10000 tons [33].

The whole fishery value chain is also impacted as fishing operations are reduced or interrupted when fisheries cannot take their boats out of the sea or due to net clogging. The revenues and sales may decrease for most fishers and vendors, while the boats maintenance costs and prices of fish increase [35]. Fish catches are reduced because of the mortality of fish and other marine life [36]. Nonetheless, the impacts in fisheries seem to be ambivalent because although the catching of the key two species, dolphin fish and flying fish, has changed, fishers have also reported an increase in biodiversity of other fish such as turpits and amberjacks [35]. Residents of islands, such as Barbados and Turks and Caicos, have fishery-based livelihoods; sargassum events affect the ability to support their household and may oblige them to spend more time at sea or work on land [35,37].

The unpleasant odors released from decomposed sargassum pose a major health risk to the local population and tourists. After 48 h on the coast, sargassum releases toxic gasses like hydrogen sulfide and ammonia as products of biomass decomposition. Effects of hydrogen sulfide on human health increase with the concentration of the gas leading to pulmonary, neurological, and cardiovascular lesions [38]. From January to December 2018 in Martinique, the mean exposure period to toxic gasses was three months. Out of 154 patients, the most frequent disorders were neurological (80%), digestive (77%), and respiratory (69%); overall, the toxicological syndrome observed in those patients was close to acute hydrogen sulfide exposure (0-10 ppm), and included eye irritation, nausea, headaches vomiting, and dizziness. It was estimated that patients living near decomposing sargassum influxes were exposed to more than 5 ppm for 50 days per year [39].

As seen, the negative impacts of the massive *Sargassum* tides transcend boundaries and are a multiregional issue that urgently needs coordination and cooperation. In 2019, during the First International Sargassum Conference and Sarg'Expo, leaders of different countries and Caribbean territories agreed to establish a "Caribbean Programme for Sargassum" with the objectives of forecasting sargassum arrivals and founding the logistics for appropriate disposal or exploitation of sargassum. The leaders recognized the need to strengthen relationships and cooperate in gathering economic and human resources to tackle the regional problem that the sargassum arrivals pose. The Caribbean Program for Sargassum is financed by the European Territorial Cooperation Fund and led by the region of Guadeloupe [40].

# 2 Sargassum composition, storage, and valorization

#### 2.1 Sargasso influx composition

As mentioned before, sargassum influxes are composed of two main species: *S. fluitans* and *S. natans*. A study carried out in six different locations of the Mexican Caribbean reported a presence ranging from 78.1 to 99.6% of *S. fluitans* and 6 to 35.9% of *S. natans* in the freshly gathered biomass. Furthermore, the collected biomass was composed of 78.1 – 99.6% of pelagic sargassum species, whereas other macroalgae and seagrasses were a minor component [24].

The chemical composition of the sargassum blooms has been previously studied in different areas (Table 1) of the Caribbean coast [24,51,52]. Pelagic sargassum species have a water content of 81 and 92%, thus dry weight content of 7 to 11% [4]. Moreover, the ash content of bulk sargassum oscillates between 18 to 24 % of the total dry weight, comprising a variety of minerals such as K, P, Na, and traces of toxic metals (As, Cd, Cu, Fe, Pb, Zn) [27,53].

In terms of organic matter, brown algae possess a minor lipid content, usually reported to be less than 5% of the dry weight [4]. However, the cell wall structure of sargassum is a source of polysaccharides like alginate and fucoidan of which the main functional groups are carboxylic groups, which are directly involved in the cation exchange of heavy metals and minerals [27,54,55]. In addition, brown algae produce metabolites such as fucoxanthin, flavonoids, phenolics, and terpenoids.

Locality /	Playa Mirador,	Playa Blanca,	Playa Xcalacoco,	Puerto Morelos	Playa Coral,	Playa Delfines,
parameter	Tulum	Akumal	Playa del Carmen		Cancún	Cancún
Geographic	20°10′19.4″N	20°24′15.5″N	20°39′43.0″N	20°50′44.1″N	21°01′29.4″N	21°03′43.3″N
location	87°26′54.7″W	87°18′33.5″W	87°26′54.7″W	86°52′35.5″W	86°48′43.9″W	86°46′ 41.7″W
Proximate compo	osition (%)					
Dry weight	$16.8 \pm 1.6$	$16.2 \pm 1.4$	$15.6 \pm 1.0$	$14.0 \pm 1.3$	15.7 ± 1.1	$17.0 \pm 1.2$
Ash	23.9 ± 1.2	23.7 ± 2.6	21.9 ± 3.1	$18.1 \pm 1.4$	19.2 ± 1.7	$20.7 \pm 0.6$
Carbohydrate	$14.2 \pm 1.3$	$14.0 \pm 1.5$	$16.8 \pm 0.9$	$17.0 \pm 2.1$	15.7 ± 1.5	$14.1 \pm 1.8$
Protein	9.9 ±1.4	$10.1 \pm 1.8$	$10.3 \pm 0.8$	$9.8 \pm 0.9$	$8.3 \pm 0.4$	$8.1 \pm 0.7$
Lipids	$2.5 \pm 0.6$	$3.0 \pm 0.6$	$3.0 \pm 0.7$	$2.7 \pm 0.7$	$3.4 \pm 0.6$	$3.3 \pm 0.6$
Elemental analys	sis (%)					
Carbon	$27.1 \pm 0.8$	33.0 ± 0.6	$31.7 \pm 0.5$	$26.8 \pm 0.6$	$31.0 \pm 0.9$	$30.1 \pm 1.2$
Nitrogen	$1.0 \pm 0.1$	$1.2 \pm 0.1$	$1.1 \pm 0.0$	$0.9 \pm 0.0$	$1.1 \pm 0.2$	$1.1 \pm 0.1$
Metals (mg/kg)						
Cd	$0.60 \pm 0.69$	$1.27 \pm 0.36$	$0.8 \pm 0.53$	$1.36 \pm 0.67$	$1.20 \pm 0.35$	$0.32 \pm 0.32$
Cu	$0.63 \pm 1.34$	<0.20	0.32 ± 0.55	$0.6 \pm 0.84$	$0.90 \pm 0.95$	$1.09 \pm 1.61$
Fe	31.46 ± 15.81	24.0 ± 6.33	54.6 ± 17.74	$31.0 \pm 8.68$	28.65 ± 4.82	25.9 ± 6.88
Pb	<0.20	<0.20	<0.20	<0.20	$0.22 \pm 0.48$	$0.29 \pm 0.33$
Zn	3.65 ± 1.53	3.96 ± 2.16	5.82 ± 3.03	$3.64 \pm 1.04$	7.2 ± 2.66	5.03 ± 1.53
As	65	40.50 ± 6.97	43.20 ± 15.61	41.10 ± 10.87	$29.0 \pm 6.24$	64.90 ± 5.29

Table 1Biochemical composition of beach-cast Sargassum biomass from sandy beaches of the<br/>Mexican Caribbean. Modified from Vázquez-Delfín et al. [24].

#### 2.2 Harvesting of sargassum biomass

Harvesting of sargassum biomass can take place on land after the biomass has reached the coast or the beach. Also, when the biomass it is still floating on the seawater. Currently, most of the harvest occurs at the beach, but harvesting at sea prevents the stranding of the biomass on the coasts and beaches and therefore prevents some of the negative impacts on the natural environment described in Chapter 1 of this report. The

different ways of harvesting sargassum biomass are summarized and described by Vos et al. [107], and best practices for sargassum harvesting in Mexico have been described recently by Chávez et al. [44].

#### 2.2.1 Harvesting at the beach

Once the biomass is stranded, it can be manually removed by operators using spades or by hand. The biomass is then transported on barrows and collected in bags or dragged on tarpaulins. This way of removal is applied to protected or small beaches with relative low volumes of sargassum, and requires sufficient availability of manpower. In addition to the cleanups paid for by hotels and resorts, there are examples where communities are getting involved. As in the case of Bonaire, through the collaboration between STINAPA and the Mangrove Maniacs [108]. On the beach, manual cleaning is preferred over cleaning by machines, because of its low disruptive level, low likelihood of disturbing sea turtle nests and a small contribution to beach erosion [107].

The mechanical removal of the biomass on the beach takes place using sifters, front-end loaders, or cane loaders (Fig. 4) [107]. These machines can be very heavy, and they could damage the ecosystem at the beach, like turtle nests, and cause compacting of the sand and removal of other plants or animals at the beach. Therefore, the access of these heavy machines to the beaches needs to be restricted to a minimum. Also, along with sargassum, much sand is collected, which causes erosion. The biomass may be removed using sifters to keep the sand on the beach and clean the sargassum, the biomass may be removed using sifters.

#### 2.2.2 Harvesting at the sea

*Sargassum* rafts are vital to the marine environment wherever they appear. These rafts provide essential habitats for many organisms (fishes, turtles, etc.) and serve as hotspots for biodiversity in open-ocean waters. Therefore, it is desirable to harvest sargassum rafts that are very close to the shore since these are more likely to strand on the coast when not harvested, and the associated fauna would be lost anyway. In addition, nearshore harvesting contributes preventing sargassum biomass from the beach on the nearby shore, thus minimizing the environmental impact on coastal habitats.

To prevent sargassum from beaching, floating barriers can be placed on the sea in front of the coast, and the biomass is harvested. To collect the floating biomass, small-scale dredging, and mowing equipment (water bulldozer) can be used, which removes the floating seaweed from the surface of the water with the help of catch arms and conveyor belts (Fig. 5). Examples of these small vessels are the "Ocean cleaner" ships [109]. The drained seaweed is then dumped in a floating transport container. Such containers have a capacity to harvest 10 to 20 m<sup>3</sup> at a time. These containers are then unloaded ashore using a crane or conveyor belt. If the *Sargassum* is harvested close to the shore/disposal area, a production rate up to 1,000 m<sup>3</sup>/day may be achieved. This equipment is not suitable to operate under rough open water conditions but is very handy under calm sea conditions close to the shore [61]. This type of ship has been used in Mexico for many years to collect *Sargassum* from impacted coastal areas.



Figure 5 Sargassum harvesting at Punta Cana (Dominican Republic). The Sargassum is kept behind barriers near the coast, and collected by dedicated ships. Source: www. algeanova.com. From [49].

Due to the negative impact of sargassum landings on tourism in the Caribbean areas, the Mexican government has invested in sargassum-harvesting ships operated by the navy [110]. These ships are 15 m long and have a capacity of 20 tons per day of biomass (it is not mentioned if it is dry or wet weight). Currently, several of these new ships are in operation in different parts of the Mexican Caribbean coast, and more are being constructed, according to the local press. These bigger ships are an addition to the small "water bulldozers" that are also active in the area for harvesting close to the shore. Chavez et al. [44] reported results on tests using different types of floating barriers and methods to bring the biomass to the beach and upload it into trucks. Collecting bands seems to be the preferred procedure to load the biomass on the trucks since it prevents contact with sand.

All in all technologies for collecting sargassum at the nearshore are very costly; as an example, the enterprise Grupo Dakatso de México has calculated that the cost of renting barriers and maintenance, monitoring, collection, and grinding of sargassum amount up to MXN \$1,800,000.00 (≈US\$87,500.00) per km of protected coastline per month [50]. Alternatives to fund the cleanup and offset the economic impact of sargassum blooms could also be the sustainable commercial exploitation of this biomass for pharmaceutical products such as fucoidans [31].

#### 2.3 Storage of the biomass

Because sargassum blooms result in large quantities of biomass arriving at the coasts in short periods, it is necessary to store the harvested biomass in a way that is still useful for further processing. When the biomass has been collected at the beach, it is crucial that it has been collected within 72 hours after arrival to avoid degradation of the material, and that sand is removed as much as possible. In case the sand content is high, it would be problematic to work with the biomass in machines.

The most used methods for seaweed biomass storage are those that aim to the material stabilization by reducing the water content or that lower the pH to prevent degradation (ensiling). Methodologies for sargassum biomass storage have been reviewed recently [49].

#### 2.3.1 Reducing water content of seaweed biomass

Seaweed biomass contains a high amount of water (up to 85% of the fresh weight); therefore, the first steps in the valorization process may include a de-watering methodology. The water content in the biomass can be reduced by:

Drying by using heat, sunlight, or freeze drying

- Letting the biomass dry extended on a surface under the sun is the most used and least expensive method for drying seaweed [111-113]. This method is both weather- and volume-dependent. Sun-drying in tropical locations may take 2–3 days in sunny weather but could take up to seven days during rainy seasons. Large surface areas are required due to the low dry matter content of the seaweed. Solar drying can cause considerable denaturalization of organic compounds in seaweed [114-117].
- Freeze drying has been used for the conservation of algae, particularly microalgae, such as *Dunaliella*, but is considered too expensive for the large-scale commercial recovery of algae and is used during laboratory-scale research and for some high-value seaweed products [116-119].
- Although coal-fired driers have been used in Ireland for the production of seaweed-meal products [120], the use of fossil fuels to dry seaweed will be costly, have a negative energy balance, and produce unwanted greenhouse gases [121,122]. However, the cost of conventional drying could be reduced if 'waste' heat is available from power generation or a large-scale refrigeration plants.

#### 2.3.2 Ensiling

This section is a modified version of a previous study [49]. Ensiling is a procedure commonly used to store agricultural products (such as grasses) during the winter season, and it can be used, as well, for seaweed storage. During ensiling wet biomass is stored under anaerobic conditions where lactic acid fermentation of water-soluble carbohydrates in the biomass occurs, causing a reduction in pH that preserves the wet biomass. Due to the special characteristics of the seaweed biomass, several challenges have been identified

that impact the effectiveness of seaweed silage. These challenges have been summarized by Milledge and Maneein [123] in a recent review, and consist of:

- High moisture content (water activity of seaweed = 0.974–0.979)
- High ash content
- High buffering capacity potential due to high anion content, which makes the pH drop to be more difficult to reach
- Varied cell wall structure that can be very different from terrestrial vascular plants
- Composition of seaweed, which can be very different from fodder crops, with different carbohydrates (alginates, laminarin, etc.) and compounds that are rarely found, or found in much lower concentrations, in terrestrial vascular plants. Examples are phloroglucinol, fucans (sulphated carbohydrates), and highly unsaturated long-chain fatty acids.

The ensiling of sargassum biomass has been reported using reusable plastic bags or barrels. As an example, *S. muticum* silage has been described by Milledge and Harvey [124]. In their study, the *Sargassum* biomass was ensiled in vacuum-sealed composite bags and stored at 20 °C for 60 days. The principal effect that was observed on the biomass was a significant reduction of salt in the ensiled biomass with a lower reduction when the biomass was chopped before ensiling. This loss of salts could be beneficial for the application of the ensiled material for anaerobic digestion, as high salt concentrations inhibit the anaerobic digestion processes. The ensiled biomass did not show reduced properties during anaerobic digestion tests compared to the fresh biomass, resulting in  $0.06-0.11 L CH_4/g$  volatile solids (VS). This result is a relatively low methane yield but is typical for brown seaweeds.

The next chapter presents the results on the use of ensiled sargassum biomass, harvested in Cancún (Mexico), for experimental tests to produce biogas by anaerobic digestion at laboratory scale at IPCYT.

#### 2.4 Current and potential applications of sargasso biomass for a valorization chain in Mexico

Valorization of sargassum is crucial for its appropriate management and different value chains have been proposed. For instance, the UNEP [36] proposes a six-step value chain (harvesting, storage, transportation, processing and packaging, distribution, and sales and marketing). Variants of this chain were proposed by Oxenford et al. [47], who provide an extensive review of the main challenges and potential solutions for the sustainable use of *Sargassum*; and by Lopez-Contreras et al. [49], who highlight the valorization of sargassum into biofuel (biogas) and agricultural products (fertilizer or animal feed supplement). This section describes the applications that can be of interest, or are currently under development in Mexico.

#### 2.4.1 Use as a source of high value macromolecules: alginate, bioactive compounds

The four principal types of sugar components in sargassum biomass are alginate, laminarin, mannitol, and fucoidan [56]. In samples of sargassum collected from Mexican Caribbean coasts, S. fluitans contained 34% DW of alginate and 8.6% fucoidan, while S. natans contained 24.7% alginate and 6.9% fucoidan; these two sugars are the only ones with a currently developed value chain for *Sargassum* spp. [21]. Alginate or alginic acid (sodium, calcium, and magnesium salts) is a linear polysaccharide composed of  $\beta$ -1,4-D-mannuronate and a-1,4-L-guluronate residues covalently bonded together and this structure can currently not be synthesized by microorganisms [57]. Nevertheless, alginate salts are widely used in the food, biomedical, cosmetic, textile, and even pharmaceutical industries due to their rheological properties. The usual extraction process of alginate from brown seaweed consists of six main steps: formaldehyde pre-treatment of the dried seaweed, acid treatment, alkali extraction, bleaching, precipitation, and drying. Alkali extraction is responsible for the yield and physicochemical properties of the final product. Once acidification generates alginate acid (insoluble), the alkali treatment dissolves alginate as sodium alginate (soluble) [58]. Currently, the Mexican enterprise Creamos Más S.A. de C.V. is dedicated to the extraction of alginate from sargassum; the extraction processes are a variation from the typical one. In Creamos Más, the fresh biomass is precooked. Then, the extraction step consists in adding Na<sub>2</sub>CO<sub>3</sub>; after centrifugation, the pellets are discarded, and soluble alginate is purified [50].

Laminarin constitutes approximately 35% DW of brown algae and is characterized by being soluble in water. Chemically, laminarin includes a linear  $\beta$ -1,3-D-glucose chain crosslinked with  $\beta$ -1,6-D-glucose attached by weak glycosidic bonds, which are easily broken during hydrolysis. Another soluble polymer is mannitol, which represents between 20 to 30% DW of brown algae and has applications in the food industry [59]. The sulfonated polymer in the sargassum cell wall is fucoidan, with approximately 20% DW. The structure of this molecule is heterogeneous and mainly consists of fucose and sulfate, along with some types of monosaccharides such as mannose, galactose, and xylose [57,59]. Fucoidans have potential antimicrobial, antitumor, antioxidant, anti-inflammatory, and anticoagulant properties; they can also be used for drug delivery [60]. This polymer can be extracted from sargassum through several processes involving hot water, diluted acid, and diluted alkali, in a series of physical and/or enzymatic treatments. As reported by Lopez-Miranda et al. [50], the Creamos Más extraction processes include the precooking of sargassum under acidic conditions, followed by the addition of Na<sub>2</sub>CO<sub>3</sub>, and finally the use of ethanol for fucoidan precipitation [50].

#### 2.4.2 Biosorption properties and applications

The sargassum cell wall is well-known for its composition rich in alginate, fucoidan, and the high number of carboxylic and hydroxyl groups distributed in the porous structure [4, 27]. This feature promotes the sorption capacity of sargassum biomass for the removal of heavy metals from contaminated effluents, particularly by ionic exchange processes. At high pH values, the carboxylic groups acquire a negative charge that can perform the ionic exchange with different kinds of cations such as heavy metals (e.g., Cd2<sup>+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Ca<sup>2+</sup>, etc.) or azo dyes. In contrast, at low pH, the sulfonic acid groups of fucoidan would serve for metal removal [50,55]. It is worth noting that sorption processes depend on variables such as pH, biosorbent amount, affinity, selectivity, and contact time [61,62].

The benefits of using the biosorption features of sargassum include minor initial and operation costs, simple design, easy operation, and no release of toxic substances. Sargasso-based biosorbents could be used for tertiary wastewater treatment, considering that brown algae can concentrate metals up to 1000 times. Moreover, the need to harvest sargasso biomass from the nearshore makes it a perfect primary local resource [55,62].

#### 2.4.3 Agricultural uses

Sargasso is regarded as a potential biofertilizer, considering the high content of minerals, water-soluble polysaccharides, and phenolic compounds of its structure, which collectively enhance soil health, quality, productivity, and even improve the immunity of certain plants [63,64]. For the direct spreading of sargassum to the soil, the contribution of nitrogen, phosphorus, and potassium should be taken into account jointly with an agronomic follow-up. Nevertheless, the main concern of applying sargassum to soils is the input of heavy metals, with arsenic heading the list. In a study conducted in the French Caribbean, the French Tropical Technical Institute recommended avoiding the direct application of sargassum to the soil due to the total arsenic contents of sargassum 100-200 mg/kg [65]. Other studies suggest using the remaining sludge from the anaerobic digestion of sargassum as potential nutrient-rich fertilizer [49,64,66,67].

Examples of commercial activities in Mexico, in the province of Quintana Roo, for the valorization of sargassum biomass, are: The company Carbonware (https://carbonwave.com/es/blog-posts/2022-02-15-say-hello-to-carbonwave/) that focuses on biorefinery of the seaweed material for products such as textiles, polymers and fertilizers and the company Dianco (http://diancomexico.com/dianco/nosotros), which also focuses on the fractionation of the biomass into products such as polymers and fertilizers.

3 Sargassum as feedstock for biogas production

#### 3.1 Introduction

Brown algae, including *Sargassum* species, could be employed as an alternative energy source, considering the concentration of carbohydrates in their structure [4,12,68]. Nevertheless, the high moisture content in sargassum (81-92%) increases the costs of processes that require dry biomass for energy generation [69]. Processes such as pyrolysis, gasification, or direct combustion are currently seen as unsuitable, considering the costs and negative impact on the energy balance [12]. As an alternative, the anaerobic digestion process can use wet sargasso as a substrate source, avoiding the drying step [70].

Anaerobic digestion is a biological process performed by anaerobic microorganisms and consists of four main steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. In this microbial-driven process, fermentative bacteria play a crucial role in hydrolyzing and fermenting complex organic waste and converting them into organic acids, hydrogen, and CO<sub>2</sub>. Methanogens, the terminal functional microorganisms in the anaerobic digestion process, are responsible for biogas generation from the fermenting step products [71]. In general terms, anaerobic digestion converts wet biomass into biogas. The main characteristic of biogas is the high methane (CH<sub>4</sub>) content (50-70%), which, after upgrading, can be liquefied and used as natural gas for energy generation [72]. Anaerobic digestion can be performed in mesophilic (32-37°C) or thermophilic (50-60°C) conditions. Generally, thermophilic digestion shows higher methane production, but mesophilic conditions are preferred due to their low energy consumption. The optimal pH of the process should be maintained in the neutral range (6.8-7.4) since acidification could inhibit anaerobic digestion [73]. As described before, brown algae have a high content of alginate and fucoidan in their cell walls. In addition, cellulose, and starchy compounds such as laminarin and mannitol are also found in macroalgae. This rich carbohydrate composition and low lignin content makes brown macroalgae a promising feedstock for CH4 production. Nevertheless, it has been reported that macroalgae biomass composition is influenced by growth aspects such as nutrients, pH, temperature, climate, or even salinity, affecting the performance and stability of the anaerobic digestion [74]. For example, Adams et al. [75] observed minimal CH<sub>4</sub> production when using spring-harvest L. digitata, in comparison to summer-harvest biomass that achieved 219 mL CH<sub>4</sub>/gVS; the improvement in CH4 was directly related to the content of laminarin and mannitol, which reached a maximum concentration in the summer season. The typical biochemical methane production (BMP) values for brown algae are between 204 to 380 mL CH<sub>4</sub>/ gVS [59]. In 2015, Allen et al. [76] reported BMP of 342 mL CH4/gVS and 166 mLCH4/g VS for the digestion of the cast brown seaweeds S. latissimi and A. nodosum, respectively.

In the case of anaerobic digestion of Sargassum spp., few experiments have been conducted reporting CH<sub>4</sub> yields of 81-104 mL CH<sub>4</sub>/g VS applying a fungi pretreatment [49]; and 541 mL CH<sub>4</sub>/g VS using a hythane (hydrogen + methane) process [77]. In contrast, the anaerobic digestion of sargassum collected at the Turks and Caicos island did not produce CH<sub>4</sub>, probably due to high phenolic content and lack of carbohydrate solubilization [31]. According to López-Miranda et al. [50], the complexity of the polysaccharides, including the degree of polymerization (e.g. alginates) and the sulfur content (e.g. fucoidans), as well as the concentration of polyphenols and salinity have a negative impact on the biochemical methane potential of raw sargasso. A possible solution consists of applying additional steps previous to anaerobic digestion. Several pretreatments could be used for carbohydrate solubilization [78]. However, a sustainable circular-economy solution is to first extract the complex polymers (alginate, fucoidan) before digestion. In this regard, the fermentation of solid residues from *S. muticum* autohydrolysis presented a higher CH<sub>4</sub> yield compared to raw material [66].

#### 3.2 Sargassum pretreatment for biodegradation improvement

As mentioned above, one of the main constraints in getting high biomethane levels from brown seaweed is the presence of insoluble fiber and polyphenols, as described by Maneein [79]. Several pretreatment methods have proved to enhance biomass solubilization and the release of fermentable sugars for anaerobic digestion [59]. To increase the reaction surface to volume ratio, size reduction of the biomass is the conventional step in macroalgae pretreatment [80]. Subsequently, a biological, chemical, thermal, or combined treatment could be performed.

Biological pretreatments incorporate microorganisms or enzymes to decompose or fractionate the macroalgae cell wall. Commercial cellulases (e.g., Celluclast 1.5L- Novozymes) or a mix of enzymes for saccharification, in combination with chemical treatments, have been used for seaweed solubilization. For anaerobic digestion, the direct addition of microorganisms capable of solubilizing the macroalgae polysaccharides was more effective than the use of enzymes, as reflected in the CH<sub>4</sub> production [70]. For example, the employment of a fungus for sargassum pretreatment increased the BMP by 20% [81]. Thermal pretreatments consist of heating the biomass directly at temperatures of 50-250 °C, promoting the disintegration of the cell wall by breaking hydrogen bonds. This type of pretreatment facilitates the hydrolysis step in anaerobic digestion, increasing the BMP. However, inhibitory compounds such as furfurals and phenols are produced when using temperatures over 180 °C [59,70].

Chemical pretreatments use a strong base or acid to improve cell wall disintegration, COD solubilization, and thus CH<sub>4</sub> production. Commonly, acids are more effective than alkalis for depolymerizing hemicellulose and delignifying biomass [59]. For acidic pretreatment, compounds such as H<sub>2</sub>SO<sub>4</sub>, HCl, and flue gas condensates with low pH values have been investigated, presenting a direct correlation between acid concentration and carbohydrate solubilization. Even though acid pretreatment is highly effective, the low final pH is incompatible with the anaerobic digestion conditions; therefore, a neutralization step is required [70]. Usually, to enhancing the efficiency of the pretreatment, combined processes are used. In the case of thermochemical pretreatment, adding diluted HCl at temperatures over 80°C intensifies the solubilization of polymers of macro and microalgae [82, 83]. For instance, hydrothermal heating with 4% H<sub>2</sub>SO<sub>4</sub> of the algae blooms from Dianchi Lake resulted in a BMP of 261.93 mL CH<sub>4</sub>/g-VS. Furthermore, acid pH promotes heavy metal desorption from sargassum, lowering the toxicity of the biomass. Studies of combined pretreatments in macroalgae are included in Table 2.

Technique	Feedstock	Reagent	Pretreatment conditions	Anaerobic Digestion process	HRT (d)	Incubation temp. (°C)	Biogas production
Thermal	F. vesiculosus	0.05 M HCI	80°C, 2h	Batch	22	37	66 mL CH4/gVS
+ chemical		0.1 M HCI	80°C, 2h	_			95 mL CH4/gVS
		0.2 M HCI	80°C, 0.5 h	_			121 mL CH4/gVS
		0.2 M HCL	20°C, 24 h		20		52 mL CH4/gVS
Mechanical	F. vesiculosus	Pressure chamber	1000 bar,	Batch	52	37	131 NmL CH4/gVS
+ Biological		1% of enzyme	50°C				
		mix of pectinase					
		and protease					
Biological +	L. digitata	Cellulase,	120°C, 1 h	Batch	32	35	243 mL biogas/gVS
chemical		2.5% citric acid	_				
		Cellulase,					219 mL biogas/gVS
		1% lactic acid	_				
		Cellulase,					176 mL biogas/gVS
		1% oxalic acid	_				
		Cellulase,					99 mL biogas/gVS
		2.5% citric acid	_				
		Cellulase,					76 mL biogas/gVS
		1% oxalic acid					

Table 2	Combined pretreatments for biogas production. Modified from Thompson et al. [59].
	combined predications for biogas production. Houned from mompson et al. [55].

#### 3.3 Co-digestion as enhancement strategy for scale-up

There are opportunities related to the implementation of sargassum anaerobic digestion on a large scale. In addition to their low BMP, sargassum blooms are seasonal and only arrive in the spring and summer months [84]. Consequently, the raw material source is limited or non-existent for the rest of the year. A potential solution for the seasonality issue consists of drying sargassum for preservation after harvesting nearshore. However, drying processes could increase costs and negatively impact the overall energy balance of CH<sub>4</sub> generation [49]. However, it has been reported that ensiling, a current technique for grass preservation, could be applied to sargassum with promising results [85].

A cost-effective alternative is the co-digestion of sargassum with different kinds of carbon-rich waste [74]. Overall, co-digestion proposes employing two or more substrates for biogas generation [86]. An improvement in CH<sub>4</sub> production has been reported by co-digesting brown algae with dairy slurry [98], cattle manure [99], glycerol [100], and food waste [87] as co-substrates. This process comprises a solution to overcoming operational challenges such as seasonality of sargassum blooms, low C:N ratio due to brown algae composition, and lack of buffer capacity of certain algae [99]. Moreover, co-digestion processes are known for being economically viable by minimizing the equipment needed and easier control of mixed waste [74]. The co-digestion strategy could improve the sargassum BMP, while at full-scale it also allows for a biogas plant that works only with the carbon-rich co-substrate when sargassum is lacking during certain seasons.

Few brown algae studies demonstrated the increase of the methane yield due to co-substrate addition (Table 3). According to Oliveira et al. [100], glycerol and used frying oil improved sargassum biodegradability with 56% and 46%, respectively as a result of the C:N ratio increment. In another work, the co-digestion of brown macroalgae *Laminaria digitata* (80% VS) and cattle manure (20% VS) produced 290 mL CH<sub>4</sub>/g VS during long-term stable operation [99]. Similarly, the use of hydrothermally pretreated sargassum (25% w) in co-digestion with food waste (75% w) resulted in 292.18 mLCH<sub>4</sub>/ g VS [87]. Even though co-digestion improves the methane production from sargassum compared with control studies, the BMP previously reported remains almost in the same range of sargassum mono-digestion, creating a gap of knowledge for co-digestion development. Note that the brown algae and co-substrate feedstock relations are variable and depend directly on both substrate characteristics [74].

The available type of waste in the region could help to select the co-substrate. In the case of sargasso co-digestion at the Mexican Caribbean, we should look up to their principal economic activity: tourism. Approximately 30-50% of the residues generated in the area are considered organic waste. The hotel and accommodation industry generates most of these residues in the form of food waste [101], which can be separated and recollected to feed an anaerobic digestion plant. This approach could provide energy for the region and solve the problems linked to sargassum blooms and food waste disposition.

Brown algae	Co-substrate	C:N ratio	CH₄ yield	Summary
<i>Sargassum</i> sp.	Glycerol/ waste	-	157 - 283	• The high carbohydrate content of glycerol and
	frying oil		mL/gCOD	waste frying oil optimized the C:N ratio and anaerobic
				digestion of Sargassum, generating 283 mL/gCOD (56%)
				and 265 mL/gCOD (46%) methane when respectively co-
				digested
S. latissimi	Wheat straw	21.6-81.6	214 - 270	A feedstock mixture of 75% macroalgae to 25%
			mL/gVS	wheat straw exhibited optimum C: N ratio of 30.2, yielding
				270 mL/gVS methane. The BMP of the optimum C:N ratio
				increased BMP of S. latissimi mono-digestion by 21%
S. latissimi /	Dairy slurry	15.70-23.40	232 - 252	• When co-digested, dairy slurry reduced the C:N
L. digitata			mL/gVS	ratio of macroalgae and promoted VFA accumulation
				• Feedstock ratio of 66:33 macroalgae to dairy slurry
				exhibited the highest methane yield
L. digitata	Green peas	-	275 - 275	• Substitution of 2% green peas with <i>L. digitata</i>
			mL/gVS	promoted VFAs formation which inhibited methanogenesis
				and rendered the digester instable. Removal of the seaweed
				from the feedstock restored digester functionality
L. digitata	Cattle manure	-	203 - 308	The optimum co-digestion feedstock ratio was
H. Sun 2019			mL/gVS	found to be 80% macro- algae: 20% manure (volatile solids
				basis), which produced 290 mL CH4/g VS during long-term
				and stable continuous operation
<i>Sargassum</i> sp.	Pretreated food	17.07-23.07	97 - 292	The maximum cumulative methane yield of 292
Thompson 2021	waste		mL/g VS	mL/gVS was obtained from a blend of co-pretreated pelagic
				Sargassum and food waste at the weight ratio 25:75

### Table 3Co-digestion of brown algae with different wastes. Modified from Thompson et al.[87].

## 3.4 Assessing the biochemical methane potential of sargassum

#### 3.4.1 Experimental strategy

An experimental strategy was developed according to the literature review previously described. Since the objective of this study was to assess the anaerobic digestion of sargassum as an alternative for biomass exploitation, a series of biochemical methane potential (BMP) tests were performed. In summer 2019, sargassum samples were collected in Puerto Morelos, Quintana Roo, México. Biomass was ensiled in zip-locked bags and stored at 4°C. After two years, ensiled sargassum was recuperated and used for the present study. To reduce the particle size, grounded ensiled sargassum was used in the experiments (Fig. 6). A thermochemical pretreatment was applied to improve the biodegradability of sargassum to evaluate the improvement on the BMP. Untreated and treated sargassum were also compared with the liquid and solid fractions after pretreatment.

The experiments were performed in the Automatic Methane Potential Test System (AMPTS II, Bioprocess Control AB, Sweden) that consist of individual stirred batch reactors (600 mL nominal volume) with 360 mL working volume. The experiments were performed at  $37^{\circ}$ C with continuous agitation (approx. 150 rpm). The gas produced in the reactors passed through a CO<sub>2</sub> absorption unit (NaOH, 3N) and the methane volume (NmL) was quantified online by the gas flow cell array of the apparatus. Granular sludge from a Tequila factory was used as the inoculum (10 g volatile solids/L) as recommended for BMP assays [88]. The first set of experiments showed the effect of thermochemical pretreatment in methane production. Subsequently, a co-digestion BMP was realized when combining different fractions of sargassum and food waste. In every experiment, alkalinity was adjusted to 3 g/L by adding NaHCO3. Mineral media as reported by Angelidaki [90] was used as a source of macronutrients. The BMP value was calculated by dividing the accumulated CH<sub>4</sub> volume by the initial total chemical oxygen demand (COD<sub>t</sub>) or VS of the substrate, determined by the standard methods [91].



Figure 6 Sargassum biomass used in this study: A) Sargassum after 2 years of ensiling at 4°C.
B) Ground sargassum after 2 years of ensiling. Photos by B. Celis

#### 3.4.2 Results

Table 4 shows the biochemical methane potential of the different fractions of the pretreated sargassum (liquid and solid), as well as the results for the untreated and pretreated sargassum. The untreated sargassum only showed 34 mL CH<sub>4</sub>/g total COD compared with the BMP of the pretreated sargassum (190.7 mL CH<sub>4</sub>/ g total COD). The pretreatment increased significantly the BMP, highlighting the need of a pretreatment before anaerobic digestion. The liquid and solid fraction obtained after the pretreatment showed BMP values lower than the complete hydrolysate and pointed out the suitability of digesting the whole hydrolysate.

Table 4	Overall results of the BMP experiments to determine the effect of thermochemic					
	pretreatment on sargassum biomass.					

Biochemical methane	Untreated	Pretreated	Liquid fraction of	Solid fraction of
potential	sargassum	(hydrolysate)	hydrolysate	hydrolysate
(mL CH <sub>4</sub> /g COD <sub>t</sub> )	34 ± 2.65	190.7 ± 27.56	115.11 ± 2.26	88.37 ± 40.78

Ensiling is a procedure that consists of storing wet biomass under anaerobic conditions where lactic acid bacteria can consume soluble carbohydrates, causing a pH decrease that preserves biomass for long periods. In the case of sargassum, successful ensiling has been performed utilizing vacuum-sealed composite bags and storing them at 20 °C for 60 days [85]. Previous studies showed that ensiling biomass did not compromise sargassum composition or CH<sub>4</sub> production. Advances in preservation techniques can help solve the problem of the seasonality of sargassum blooms [64,93].

The complete hydrolysate improved the BMP, compared with the untreated sargassum and the isolated liquid and solid fractions. Therefore, there is no benefit in separating the liquid from the solid phase of the hydrolysate. The methane potential of brown algae depends mainly on carbohydrate consumption [94] and chemical pretreatments showed that the addition of a strong acid accelerates hemicellulose depolymerization and delignifies biomass, releasing sugar [95].

The hydrolysate generated by the pretreatment of sargassum contained 44.51% of soluble COD, and according to the literature the polysaccharide structure in the remaining solids changed and increased the bioavailability of carbohydrates [96]. The results showed that the high salt concentration in the liquid hydrolysate experiment could compromise the BMP performance. However, the neutralization step cannot be avoided because the acidic pH (< 5.5) produces anaerobic digestion inhibition [97].

Thermochemical pretreatment increased the BMP of sargassum by 82.10 %, which can be compared with the 81.72% improvement in the methane yield reported by Thompson [92] when using a high-pressure hydrothermal pretreatment (30 bar, 140°C, 30 min). Even though high-pressure pretreatments are successful and do not require the addition of chemicals for hydrolysis or pH adjustment, they create a vast energetic demand that reflects directly in the economics of the process. In contrast, the thermochemical pretreatment is not only effective in terms of COD solubilization and CH<sub>4</sub> production but also offers an easy

operation, low energy demand technique, which can contribute to make the sargasso energy generation a cost-effective process [70, 89].

The addition of food waste as co-substrate increased de BMP. With a 50:50 ratio of sargassum and food waste, the BMP was 780.76  $\pm$  34.44 mL CH<sub>4</sub>/g VS, which is a 4.5-fold increase compared with 100% pretreated sargassum digestion (173.36  $\pm$  25.05 mL CH<sub>4</sub>/g VS). The co-digestion of sargassum with food waste could be a suitable option since tourism is the central activity in the Mexican and other states in the Caribbean, the hotel and accommodation industry contribute greatly to the organic residues generated in the region [101], positioning food waste as an appropriate substrate for this study. The fractions of sargassum and food waste were selected according to previous algae co-digestion studies [102]. These results are preliminary and would be presented in a scientific publication.

### 4 Anaerobic digestion of Sargassum biomass at large scale

## 4.1 General introduction to large scale anaerobic digestion processes

As mentioned above, the anaerobic digestion of organic wastes to methane (also called methanisation) has a long history and during the last four decades this technology has been developed and implemented at industrial scale. This process is a natural way of decomposing organic waste, producing gases and stabilized fibre structures. Peat is the product of a time lasting rotting process under swamp conditions, in which the available oxygen (making the process circumstances anaerobic) is converted into carbon dioxide gas and other liquified carbon molecules are processed to methane gas. Certain small amounts of ammonia gas (NH<sub>3</sub>) and hydrogen sulphide (H<sub>2</sub>S) are produced as well following the Buswell and Boyle formula:

$$C_{n}H_{a}O_{b}N_{c}S_{d} + \left(n - \frac{a}{4} - \frac{b}{2} + \frac{3}{4}c + \frac{d}{2}\right)H_{2}O \rightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}c + \frac{d}{4}\right)CO_{2} + \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3}{8}c - \frac{d}{4}\right)CH_{4} + cNH_{3} + dH_{2}S$$

The digestible organic matter (C, H, O, N, S) in the organic wastes is converted into gases, while the non-digestible fibers (including lignin-based polymers) form the stabilized fiber. These fibers can be broken down further by biological activities of fungi and bacteria under aerobic conditions by a composting process. The methanisation of manure, especially in slurry form is probably the basic for the development of the methanisation technology. Logically this way of rotting under anaerobic conditions of a slurry type substrate made the processing of less liquid substrates into a challenge of mulching and dilution. First the methanisation of wastewater treatment (WWT) sludge was brought into practice, a processing quite similar to the processing of animal slurry.

Nowadays, anaerobic digestion processes focus on the use of residues om the production and processing chain of food and feed as feedstocks for energy and organic fertilizer production. The use of co-substrates, especially the more concentrated organic products have put the basic technology of mulching and dilution under discussion, because the addition of liquid (water) to dry substrates like corn silages, corn straw or organic municipal waste, brings the need of larger reactors and liquid streams are produced that need to be processed and stored after methanisation. To understand this development it should be realized that the methanisation process is a combination of mechanical and biological sequential processes, where the result of an earlier step the start is for a next step as shown in Figure 7.

The typical steps of an anaerobic digestion plant are described below:

The first step of the process is the mechanical mashing of the feedstock. Here the goal is to crush the cells in the feedstocks so that organic components become accessible to bacteria and eventually enzymes used for liquefaction. Vegetal cell walls are mainly formed by long chain fibers, which structure is only slowly hydrolyzed. For example straw ploughed into the soil can be found in that soil during some follow up years. After the mashing the substrates can be mixed with other substrates and the process can start with hydrolysis. This is a process where acids are produced and the pH will decline. The bacterial activity is high under these circumstances and short chain organic acids are produced. The pH will go to values of less than 5,4 and no methane is produced, because methanogenic bacteria hardly function under these acid conditions.

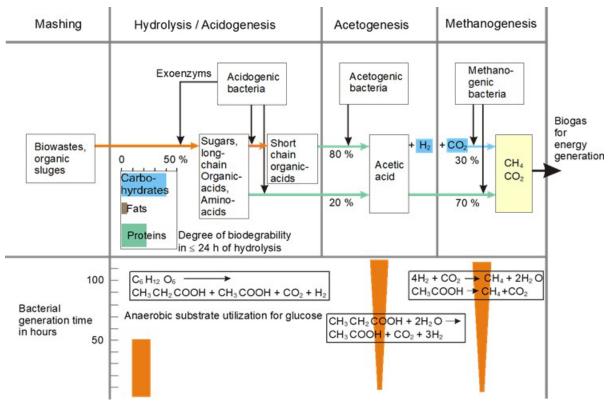


Figure 7 Scheme of the methanization process

In principle, if the concentration of fresh substrates fed into a complete stirred reactor is above a certain level, the process will stop after hydrolyzation, because the acidity is down to silage conditions (about pH 4) and no biogas will be produced. This represents a problem using fresh biomass for methanisation, where its technology has been developed with organic waste, like manure, which is completely hydrolyzed during the digesting process before in the animals. So the use of one simple reactor for the whole process is less likely if substrates are fresh or arrive from a silage conservation.

For this reason research, empiric most of the time, is needed to develop process technology for the processing of fresh (non-pre-digested) organic substrates. For different types of substrates, separate processing steps are needed, and reactors could be run in batch or continuous mode.

Temperature can play a role in the methanisation process, In some cases, higher temperatures could have a beneficial effect on the gas production, but this is not always the case. A strategy to regulate the temperature in the reactor could include adapting the temperature of the substrates to be fed during the duration of the process. This complex, industrial approach for a continuous anaerobic digestion process requires automatized control.

## 4.2 Considerations for the anaerobic digestion of sargassum biomass at large scale

In this section, suggestions, and restrictions with regard to the methanization of sargassum biomass are described. Two important aspects need to be considered when using sargassum biomass as feedstock in industrial anaerobic processing installations:

1. The availability of sargassum over a long period. Tests have shown that Sargassum can be ensiled, indicating that sugars to stimulate acidification under low or no oxygen conditions are available from the material as such. Further research and tests should demonstrate the possibilities and eventual necessities of additional sugar, acids, and or mechanical treatment before and at ensiling. Ensiling would facilitate the availability of the substrate over a long period.

2. Availability of alternative substrates and co-substrates. Other fresh, high concentrated organic waste or by-products that are available over a long period, may function as co-substrates or even

replacement substrates for Sargassum to make use of the treatment installation when sargassum biomass is not available.

Once the above-mentioned aspects on availability of feedstocks are met, a facility for methanisation would consist of the following steps and sections:

- Reception, mixing and dosage equipment
- Mashing, so that vegetal cells are opened, cell walls crushed
- Separated hydrolyzation process step
- Separated methanization step
- Digestate treatment, handling and storage equipment
- Gas buffering and conversion to electricity and heat
- and/or Gas compressing and distribution
- Gas cleaning and injection into a methane gas grid
- Automated process management
- Security systems for over/under pressure and biogas handling

Based on the estimated quantities and the qualities the necessary capacities (volumes) can be calculated. Pricing of installations and their products will finally show the economics of the processing facility. A preliminary process scheme and basic technology choice can be made based on earlier results and experiences as described before.

The scale of the process will influence the type of facilities to be implemented. As an estimation, for the processing of quantities up to 15 ton biomass feedstock per day containerized small scale equipment could be used. An example of these type of facilities is the Bioblocks system developed by AllOptimal If larger quantities of feedstock are involved permanent concrete-based constructions are to be realized. In principle quantities are not restricted, and modular systems could be used in case that the amount of feedstock would fluctuate in time. In the case of designing a plant for co-processing sargassum biomass with organic residues for anaerobic digestion, the (variation on the) availability of sargassum will have to be taken into account. In view of this, modular and flexible systems for methanisation could be an interesting option.

The basic technology as used by AllOptimal for installations for the processing of stackable substrates comprises of the following process steps:

- Stationary Buffer-mix container, from which feeding of a collision mill and solids pump are fed
- Hydrolyzation tank reactor with heating
- Plug Flow methanization reactor, with heating, biogas collection, over/under pressure security, stirring
- Digestate degassing and separation of fractions, storage and postdigestion of the liquid fraction
- Biogas storage and collection from main reactor and from liquid fraction storage
- Biogas treatment: de watering, H<sub>2</sub>S cleaning, cooling, security by burning of surpluses, etc.
- CHP installation with grid connection
- Automated management system

Examples of installations using technologies developed by AllOptimal are: Centre de valorisation des déchets organiques a Lille, https://www.youtube.com/watch?v=rfOkebV6Ed8&t=276s (2005 – 2007), and Abfallentsorgung Kreis Lippe, Lemgo, Germany, https://abfall-lippe.de/abfallsorten/biomuell/ Linde-BRV 2000, 50.000 ton/year, Methanisation and composting. Also, studies on co-digestion of sargassum biomass with organic residues have been carried out by AllOptimal in collaboration with other partners.

### Vermicomposting of Sargassum biomass

5

Vermicomposting is a process that uses earthworms to transform organic residues into a secondary product named vermicompost [104]. Vermicomposting in Mexico started around the 1980's when the first studies on the degradation of coffee pulp through the use of earthworms were carried out at the Institute of Ecology in Xalapa, Veracruz. The technology was imported from the United States where Mary Appelhof carried out vermicomposting with the red earthworm *Eisenia fetida*. These practices began to be widely used in California, and from there on the earthworms were called the red Californian earthworms, while those earthworms have an European origin. In Mexico, vermicomposting has become widespread for the management of household and agro-industrial organic waste.

The use of vermicomposting for the transformation of the sargassum into fertilizer material has been little explored. Due to the natural characteristics of the sargassum such as high salt concentrations, a pre-treatment is required before being processed for composting or vermicomposting. Ananthavalli et al. [105] have found that 15 days pre-treatment helps on the sargassum stability and then the vermicomposting occurs with mixing 1:1 sargassum with cow dung. This research was done using a tropical earthworm *Perionyx excavatus* (Perrier). The properties of the resulting fertilizer were improved by vermicomposting compared with the traditional composting method, i.e. the pH was near to neutral, potassium, phosphorus, magnesium and calcium were higher after the vermicomposting process and also the C/N ratio of 14 was much better for soil conditions than the C/N ratio obtained by composting.

Vermicompost is seen as a promising material for crops. Several studies claim that vermicompost accelerates seeds germination, and plants grow more vigorous and are resistant to diseases when vermicompost is regularly applied. A combination of 30-50% vermicompost at soil volume enhances positive effects on plants [104]. Moreover, from the vermicompost technology it is possible to extract enzymes which can accelerate the degradation of high volume agro-industrial wastes [106].

Sargassum vermicomposting has not been yet developed in Mexico, probably because of the high transportation and pre-treatment costs. Normally vermicomposting is carried out on farms where the waste is produced locally, or in case of household organic wastes. With respect to sargassum, it is important to implement pre-treatment and vermicomposting facilities near the coasts where this is harvested.



*Figure 8* Vermicomposting tests using sargassum and paper. Left: the worm Eisinia fetida. Right: mixing sargassum with paper for the tests

In this study we tried to address two main applications for sargassum biomass in the terrestrial environment, 1) as an organic fertilizer, testing if it can be ingested by earthworms in vermicompost, when recycling the material, alone or mixed, and 2) as a direct fertilizer for nutrient supply to the soil.

Five different experiments were set up, with different mixtures and concentrations of dried sargassum (from 0.1% to 100% (fresh weight percentage in the mix), with horse manure, sandy soil, pot soil and paper). Two different samples of sargassum were used in this study, one harvested at the coasts of Florida and one harvested at Bonaire. The composition of these samples is described in a previous report [49].

In the experiments with sargassum used as a nutrient supply (Fig. 8, 9), the worms all died, despite the fact that the sargassum was treated beforehand (removal of salts, thorough washing with fresh water).

The treatments where sargassum was mixed with paper at different concentrations (0-70% sargassum) were more successful. In these experiments earthworms belonging to the species *Eisenia fetida* ingested sargassum during 2 months. The percentage of mortality was inversely dependent on the concentration of sargassum, finding the lowest mortality (10%) with 70% sargassum and 30% paper. These results are very preliminary, and further studies are needed in order to fully characterize the use of sargassum as a co-substrate in vermicomposting by this earthworm.



Figure 9 Different mixtures of sargassum and paper

# 6 Sargassum application in the construction industry and nanomaterials

#### 6.1 Sargassum in construction

According to a recent literature review, the process of understanding the potential applications of sargassum in construction requires a stage for identifying the components present in the algae. Studies agree that the composition of sargassum changes according to its geographical location, season, and related environmental factors [125-128]. Therefore, composition studies have been carried out for Mexican Caribbean Sargassum; finding that, although there is information on chemical composition and concentration of micro and macromolecules of the algae of Mexican Caribbean coast, there is a lack of data on the biotechnological application to the construction industry [129]. The effort to use sargassum as a component in the development of materials has started in Mexico, it has been included in the pavement as fibers and additives, the addition of sargassum at different concentrations between 0.5 and 4% wt increased the permanent deformation factor (G\*/sin $\delta$ ), and higher elastic behavior is reached [130,131]. The incorporation of sargassum as a component of construction blocks was implemented in 2019 by SargaBLOCKTM; this company is manufacturing blocks for the construction of houses. Blocks are composed of between 40 to 60% of Sargassum and compressed by hand in an artisanal way and mechanically applying a force of 112 kg x cm<sup>2</sup> [132].

Sargassum is a marine source that can be incorporated in Portland cement composites (ash, fibers, and additives) [133-135], and in the polymer composites (fibers) [136], adobe (fibers and additives) [137,138], and mortars or facades [139]. The mortars are of great importance to the construction industry because they are related to the thermal comfort in the house and energy consumption that mainly affects user's economic loss. In this sense, the Sargassum has a thermal conductivity of 0.045 W m-1K-1and a specific heat value of 2000 J kg-1K-1, which are lower than 0.07 W m-1K-1and greater than 1400 J kg-1K-1, the limits to consider one material as a thermal insulator [139].

Sargassum can also be used in the construction of panels, as it was implemented using the seaweed *Posidonia oceanica* in Greece (MDF and particleboards) [140,141]. Regarding the thermal insulation properties, it is possible to modify mortars with thermal properties by adding Sargassum as an alternative material, called bio-insulators or thermal mortars. From this point of view, a new current of research is opened based on the potential use of sargassum, obtained from the massive arrival on the Mexican Caribbean coast, in technological applications, attacking vulnerable issues of national interest with a social benefit.

#### 6.2 Nanostructured Materials

Pelagic Sargassum chemical composition opens the opportunity to develop new nanostructured tailored materials for multiple applications, such as energy generation [142,143], medicine [144], antibacterial agents [145,146], and environmental remediation tools [147,148]. Recently, nanocarbons materials have been produced from brown sargassum for their use in electrochemical systems such fuel cells as [142] and supercapacitors [149], where the algae was activated at different temperatures presenting high specific surface areas <2500 m<sup>2</sup>/g. In the case of the alkaline fuel cell, the oxygen reduction reaction parameters of the nitrogen-doped carbon show comparable results with the traditional Pt electrocatalyst material [142]. Activated carbons from sargassum in supercapacitors also presented high specific gravimetric capacitance, good rate capacity, and excellent cycling stability near 95% [149]. Hence, nanocarbons from pelagic Sargassum has also been used to synthesize metal nanoparticles. Silver nanoparticles were obtained from extracts from *S. natans* and *S. fluitans* [146] and *S. muticum* [145], having a particle size distribution between 20 to 50 nm. The Ag nanoparticles studies demonstrated high performance as an antibacterial

agent. Magnesium oxide [150] and zirconia oxide [151] nanoparticles were synthesized using *Sargassum wighitii* as the reducing and capping agent. MgO nanoparticles show high performance and not only have antibacterial and anti-fungal but also shows strong cytotoxic activity against lung cancer cells. On the other hand, ZrO<sub>2</sub> show antibacterial effect over the following bacteria: *Bacillus subtilis, Escherichia coli*, and *Salmonella typhi*.

# Governmental policies and advice to deal with Sargasso in Mexico

7

In 2015, the tourism industry of the Mexican Caribbean hired approximately 5000 temporary workers to remove the seaweed from the main beaches, and the federal government allocated US\$3.2 million for sargassum harvesting [30,34]. However, only ~10% of the coastline was considered essential for tourism, leaving the rest of the beached seaweed to decompose in the area [9]. To standardize the efforts to contain and remove sargassum, Mexican authorities promulgated in 2021 the "Technical and management guidelines for attention to the contingency caused by sargassum in the Mexican Caribbean and the Gulf of Mexico" [41], a document. In this document, the guidelines are structured in eight chapters:

- 1. Gathering in the marine and coastal zone. The recollection should be selective to ensure that specimens of marine species at risk or with some protection statuses are not caught accidentally. Recollected sargassum cannot be returned to the sea.
- 2. Containment and removal in barriers. The location of the containment barriers will depend on the coastal and oceanographic characteristics of the seabed of the reef barrier, seagrass meadows, as well as the patterns of currents, winds, and tides to increase their effectiveness and reduce impacts on the environment. Barriers should be temporary; they can be installed only when sargassum blooms appear nearshore.
- 3. Removal from the beach. It should be performed in the first 72 h after sargassum arrived. Light machinery could be used if it doesn't modify the natural characteristics of the site.
- 4. Comprehensive management. Collected sargassum could be disposed of in the official area containers. The gathering stations should be assembled with an aeration section and a lixiviate disposition system, to minimize contamination of the region.
- 5. Recommendations on health and safety in the handling of sargassum. The personnel who carry out activities in contact with sargassum must wear the appropriate equipment, which includes gloves, boots, and masks, to control the risks of exposure to hydrogen sulfide.
- 6. Management of sea turtle nesting beaches. The NOM-162-SEMARNAT-2012 must be followed. In addition, the use of any type of machinery is forbidden in the dry zones of the beach.
- 7. Monitoring of the volumes of sargassum collected on the coast. For the purpose of monitoring, all sargassum harvesting work will be reported online.
- 8. Possible uses. For exploitation, sargassum can be collected in the open sea, nearshore, and ashore, attending to applicable regulations for each case.

Not all the Caribbean states have national frameworks for the management of sargassum tides, and some regional guidelines have been developed through the last decade once the recurrence and magnitude of the problem were understood.

Most of the actions taken so far have been adaptative and go in the directions of prevention/cleanup and reuse. These actions can be categorized as forecasting, collection and disposal, or harvesting and reuse [36]:

**Forecasting** is essential for the coastal communities to timely prepare for sargassum arrivals and set up plans for collecting and disposal or to predict the supply of sargassum for reuse. For short time scales (one week), satellite imagery and operational 7-day ocean current forecast are enough to predict beaching events [42]. On larger-scale forecasting, early warning systems need to combine satellite imagery, drifters, remote sensing, and modeling. Recently, the SARTRAC (Teleconnected SARgassum risks across the Atlantic: building capacity for TRansformational Adaptation in the Caribbean and West Africa)-Ensemble Forecast System was useful to provide early warnings for Jamaica at a seasonal timescale (180 days). The system algorithm also accounted for growth, mortality, and sinking [42]. Nonetheless, the system was limited by the availability of quality satellite imagery, which is still a challenge for all forecasting systems relying on satellite coverage. Other issues of forecasting systems include the lack of consistent national and site-level monitoring of sargassum quantities to validate the models, as well as the high cost of precision satellite imagery to predict the presence of sargassum locally, among others [43]. Table 5 presents a list of non-commercial warning systems of public access.

Name of the	How sargassum is monitored	Output	Region covered	Web page
forecasting				
system				
SEAS	Satellite imaginary NASA (Modis/Terra,	Information bulletin	Caribbean Sea and	https://optics.marine.
(Sargassum	Modis/aqua, Landsat, VIIRS). Images	with the general	Gulf of Mexico	usf.edu/projects/saws
Early advisory	are processed through a virtual	outlook for current		.html
system)	antenna system to obtain floating algae	bloom condition and		
	index (detects floating algae and other	future probable		
	materials on the ocean surface) and	condition.		
	color index (traces ocean circulation			
	features).			
CERMES	Validated sargassum transport model	The bulletin provides	Eastern Caribbean	https://www.cavehill.
(Sargassum		medium time scale (3		uwi.edu//cermes/proj
Outlook Bulletin		months) island scale		ects/sargassum/outlo
		forecasts		ok-bulletin.aspx
SIR (Sargassum	Uses AFAI (Alternative Floating Algae	Provides and overview	Caribbean and Gulf of	https://www.aoml.noa
Inundation	Index) fields generated by the	of the risk of	Mexico	a.gov/phod/sargassu
Report)	University of South Florida, the	Sargassum in the		m_inundation_report/
	algorithm analyzes AFAI values in the	shoreline, the risk is		
	neighborhood of each coastal pixel and	classified as low,		
	computes the difference of those	medium, or high		
	values and a multiday baseline.			

Table 5 Non-commercial warning systems to forecast the presence of Sargassum.

**Collection and disposal** of beached sargassum was the first action that several Caribbean states took. Hotels and resorts are the most active economic sectors involved in this action, the majority use manual raking and shoveling, and others may also use heavy machines (front and cane loaders, Fig. 4). Despite the fact that heavy-machines can collect large volumes of beached sargassum, this should be the last option because of the enormous detrimental impact that they cause to the beach. Sand is compacted, which affects turtle nesting and endangers other species (crabs, sand dwellers, plants); also, huge amounts of sand are removed causing beach erosion [37,44,45] and hotels and resorts must then invest in equipment for sand recovery [44]. Manual collection of the beached sargassum is the preferred method to avoid the negative impact, but it requires a lot of workers that could be exposed to the health risk that decomposed sargassum poses.

Currently, the consensus is that burying the collected *Sargassum* on the beach is not a good idea due to the toxic and corrosive hydrogen sulfide produced. Several guidelines suggest disposing of the collected sargassum appropriately, and several Caribbean states designated areas for landfilling it. The problem is that some sites are not lined to contain appropriately and as such they permeate down to the aquifer very easily due to the karst nature of some Caribbean regions [44,46]. Another negative issue is the need of clearing land to create landfills, which jeopardizes land-based ecosystems. The truth is that there will not be enough space to dispose of all the amount of sargassum that reaches the coast, leaving us only one option: to take advantage of it like a commodity.

**Collection and harvesting nearshore seem to be the best option** for using sargassum as a valuable resource in a more sustainable way than collecting it at the shoreline, minimizing environmental damage [47]. In some places, hotels, resorts, and governments have opted to place barriers (booms) to stop sargassum from reaching the coast. From there, sargassum may be collected using a series of machinery and specialized vessels with conveyors and catch arms that come in several sizes and prices. Companies such as Algeanova and The Ocean Cleaner, offer integrated solutions for barriers and boats (Algeanova, The Ocean Cleaner). The most holistic solution so far was considered in 2019 by the Dutch partnership Damen-Maris. The idea was not only harvesting the sargassum but also pre-processing it on board (drying and ensiling) for anaerobic digestion once on land. The group was going to present the advances of this solution at the 2019 SargExpo in Guadeloupe; regrettably, there was no more news about it.

**Regional collaboration is crucial to address sargassum management successfully**. Due to the complexity of the problem and the different stakeholders that should be involved (governments, scientists,

private enterprises, entrepreneurs, and local communities), one of the main challenges with harvesting sargassum for further use is the lack of governance to support the valorization of the algae, particularly by large-scale enterprises. Despite the significant increase in research, data, and management strategies, there is still a lack of regional public policies, norms, protocols or standards that regulate who can have access to the resource, how, and when [36, 47, 48]. Solving this problem will require active participation and commitment of all stakeholders, with a great dose of participative decision-making at local and regional scales.

# 8 Plans for follow up and possible funding programs

#### 8.1 Plans for follow up: analysis of potential value chains

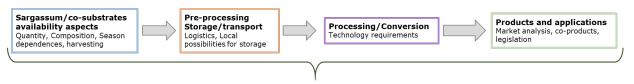
A major part of this report consists of the compilation of data on sargassum origin, policies, management and uses from a variety of sources, with a focus on the Mexican situation. We have consulted scientific literature, (governmental) public reports, internet resources and discussed with parties involved in sargassum research or utilization. In addition, experimental tests have been carried out on the use of sargassum biomass for two applications that are considered to have the potential to be useful in the Mexican situation:

- Production of biogas at laboratory scale by anaerobic digestion of pre-treated sargassum biomass as such or in combination with food waste. The results of these tests are very promising. Considerations to be taken into account for upscaling this process using sargassum as a (co)feed have been given by All Optimal b.v., which has extensive experience on commercial anaerobic digestion plants.
- 2. Preliminary tests on the use of sargassum biomass as the substrate for vermicomposting. The results of these tests show that worms could grow on sargassum mixed with old paper.

To further investigate the potential of any of the technologies described in this report to be implemented at the commercial scale, a **value chain analysis needs to be carried out**. In this value chain analysis, data need to be compiled or generated that would enable interested parties and stakeholders to evaluate the sustainability, economic and social impacts of such a process.

Anaerobic digestion is a technology that already is widely implemented to produce biogas for use as an energy carrier, and the digestate produced could be used in agriculture (if complying with the relevant safety regulations) or for uses outside the food chain. Adaptation of the existing technologies for anaerobic digestion of organic wastes will be required to accommodate the sargassum biomass as well. A certain degree of flexibility of the system will be required with respect to working volumes and applications of the digestate, since the composition and availability of sargassum are expected to vary. Also, storage could lead to a stable source of sargassum biomass throughout the year.

The different steps of such a value chain have been already briefly mentioned above, and include: sourcing of feedstocks (Sargassum, organic wastes), logistics and storage, processing of biomasses to products, product evaluation, markets, and overall sustainability, social and techno-economic impacts (Fig. 10). For the Dutch Caribbean situation, a detailed plan for assessing value chains and knowledge gaps was published recently [49] and although some steps in these chains could apply to other areas, for each situation the value chains need to be adapted taking into account the local conditions, such as the socio-economic situations, logistics, markets for the feedstocks and products, current uses of the feedstocks, environmental impacts or the development of the industry at the local level.



Sustainability, environmental and societal impacts of the complete chain

Figure 10 Generic scheme of a value chain using sargassum biomass as co-feedstock. The impacts on the environment, sustainability and society of the harvesting and use of sargassum for the specific applications (in agriculture, as source of materials, etc.) needs to be evaluated prior implementation of the processes Since 2019, the Polytechnic University of Quintana Roo (UPQRoo), located in Cancún, has worked on the identification of sustainable technologies and business opportunities utilizing sargassum biomass that could lead to implementation in the area, or in other areas in the Caribbean. This work was financed by Mexico's Science and Technology Council (Consejo Nacional de Ciencia y Tecnología (CONACyT)) [45]. In a recent publication, Oxenford et al. [47] make a very complete description of the state-of-the-art of the challenges and knowledge gaps that need to be addressed before value chains can be built based on sargassum. The value chains that could be feasible depend largely on the infrastructures and market characteristics of the specific area of implementation, therefore for each area such a value chain analysis has to be performed, as a basis for implementation plans.

As a follow up of this study, a project to evaluate the uses of sargassum biomass for biogas production together with food wastes could be an option. For the evaluation of such a value chain, a suitable area needs to be chosen were sargassum is available at sufficient quantities or were it can be stored in a convenient way. The possibilities of the implementation of a new process, or to upgrade existing process need to be evaluated as well, and also the economic viability based on the revenues obtained from the product

#### 8.2 Stakeholder analysis

The management of sargassum blooms and beachings involves a great number of stakeholders, as blooms appear in large geographical areas, with negative impacts on many aspects of the affected communities: the environment, the economics, and many others. Because of the importance of these issues, Sargassum is one of the subjects treated by the Caribbean Environment Programme (CEP). This program was established by the United Nations Environment Programme (UNEP) in 1981, as one of its Regional Seas Programmes in recognition of the importance and value of the Wider Caribbean Region's fragile and vulnerable coastal and marine ecosystems including endemic plants and animals. On the UNEP-CEP website (https://www.unep.org/cep/), several factsheets and other reports about sargassum are available.

Several recent reports have made stakeholder analyses of the involved parties in sargassum blooms from different perspectives. For the Dutch Caribbean situation, stakeholders involved in valorization chains were summarized by Lopez-Contreras et al. [49]. In a broader context, a recent UNEP report [36] describes a stakeholder map that is structured around three broad categories, namely:

- Stakeholders responding to sargassum influxes as a hazard requiring management, mitigation, or adaptation
- Stakeholders responding to sargassum as a resource/ commodity/ opportunity
- Stakeholders with broad interests in sargassum in terms of both hazard management and potential opportunity

Each of these broad categories is further sub-divided into sectors, e.g., tourism, fisheries, etc., and stakeholder organizations in each category/sector are identified across the public and private sectors as well as the NGO/CSO community. Several actors working at the marine science-policy interface in the Caribbean are featured in the stakeholder map. Of notable mention is the UNEP-CEP's Specially Protected Areas and Wildlife (SPAW)- Regional Activity Centre's (RAC) role in engaging regional stakeholders and facilitating networking opportunities related to sargassum management and research. In the white paper, many of these initiatives and partners are featured, and some are described in the appendices. Section 8 of the UNEP white paper outlines the contribution of the SPAW protocol to the regional sargassum management strategy in more detail.

In their study, Oxenford et al. (2021) [47] consulted a wide diversity of stakeholders worldwide, to identify challenges and opportunities in the value chains. For the Mexican situation, the stakeholders described are listed in Table 6. In this table, a listing of stakeholders is shown. In Mexico several, mostly small, companies are active in the development of products based on sargassum as feedstock, or active in the development of equipment or ships for harvesting. Innovations on the uses of sargassum in materials or production of biogas are carried out at universities and research institutions. The ecological and environmental impacts of the sargassum blooms are being studied by universities and research institutions, often in collaboration with international partners.

## Table 6Stakeholder groups in sargassum valorization chains in Mexico. Modified from<br/>Oxenford et al. [47].

Stakeholder category	Sargassum related product	Comments
Private sector	Products from Sargassum:	Most of these stakeholders are
	Materials: Bioplastics, paper and cardboard, construction blocks,	small and medium enterprises
	Activated carbon, shoes	
	Energy applications: Biogas, pellets for combustion	
	Agriculture: fertilizer supplement, compost, mulch,	
	High value products: alginates, fucoidans	
	Products related to sargassum harvesting:	
	Floating barriers, harvester boats, beach clean-up equipment	
Private sector consortium	Sargassum boat, floating barriers, active member of the Puerto	
	Morelos Protocol on sargassum management	
Research group	Products from Sargassum:	Universities include: UNAM,
	Animal feed	Universidad Autónoma del Carmer
	Crop production (mushroom substrate)	
	Biogas	Research institutes include:
	Materials	TECNM / Instituto Tecnológico de
	Related subjects:	Cancún, Instituto Potosino de
	Eco-toxicology of sargassum leachates	Investigación Científica y
	Biodiversity	Tecnológica (IPICYT), Centro
	Sargassum physiology	Interdisciplinario de Ciencias
	Uses in purification and bioremediation, biofilters	Marinas del Instituto Politécnico
		Nacional, Instituto Tecnológico de
		Chetumal, Centro de Investigaciór
		Científica de Yucatán, Parque
		Nacional Arrecife de Puerto
		Morelos
Public institutions	Legislation, sustainable mitigation plans, funding fundamental and	See Chapter 6 for roles of public
	applied research on sargassum origin, prevention and uses	institutions

### 8.3 Potential funding sources for Sargassum-related projects

In the areas and countries where the beachings and blooms are causing the most impacts, mitigation plans are in place or being developed. These plans focus on preventing the landings of sargassum or on the biomass removal from the beaches and coastal areas. In most cases, the sargassum biomass is considered a waste material and is primarily being discarded or landfilled.

The development of value chains toward the use of sargassum biomasses requires research efforts to fill in the gaps in knowledge on the different steps in the value chains, since sargassum biomass is a relatively new feedstock type of. To speed up the development of these value chains, some strategies that governmental institutions can follow to support innovation by local enterprises have been identified [45, 47] and are summarized below:

- Support innovation by small and medium enterprises by creating funds that are easily accessible to entrepreneurs
- Create incentives for valorization options in the affected local areas
- Enhance networking between stakeholders by creating hubs, shared facilities, or other means

Besides national and local programs to stimulate innovation, designating international funds for collaboration and development is advised. The sargassum blooms affect a large number of countries, islands, and areas around the Caribbean sea, and alliance will enhance the exchange of knowledge and speed up innovations. Examples of such programs could be:

- Programs similar to the UNDP program, where different countries can apply for funding for sargassumrelated research
- European programs that include countries in the Caribbean region

• Establishing programs for education, research, and development in collaboration between countries and regions affected by the sargassum problems

# 9 Conclusions

From the information described in the different chapters of this report, several conclusions can be made:

- In Mexico, there are many activities related to sargassum harvesting, valorization, and innovations.
   Most of these activities are being developed by small companies and entrepreneurs, and they are still not implemented on a larger scale. At universities and research centers, there are activities on innovations and fundamental research.
- During recent years, knowledge on the management of sargassum biomass and mitigation plans to minimize impacts have been developed. However, this knowledge needs to be further translated into standard protocols and implemented in the affected areas.
- Preventing the arrival of the sargassum biomass to the coasts and beaches is a way to reduce the negative impacts of the blooms. When harvested nearshore, the sargassum biomass does not get contaminated with sand, making subsequent treatment, storage, and logistics less complex, and making valorization possible.
- From the results obtained during this project at IPICYT, we can conclude that sargassum biomass can be kept stable during long periods using an ensiling-type of storage. This study shows the effective use of a thermochemical pretreatment to improve methane production from a two-year ensiled sargassum sample harvested in Cancún, and the successful co-digestion of pretreated sargassum with food waste. The relatively high BMP values achieved in the present investigation (780.76 ± 34.44 mLCH<sub>4</sub>/gVS) when using a combination of 50% pretreated sargassum and 50% of food waste, show the potential of this approach. All Optimal BV is experienced with the requirements and considerations when scaling up an anaerobic digestion system that includes sargassum biomass as (co-)feedstock.
- Preliminary tests on the use of sargassum biomass as a substrate for vermicomposting carried out by WUR, show that worms could grow on sargassum mixed with old paper. This application needs to be further characterized, but the first results are promising.
- Implications related to the high salt, heavy metal, and arsenic content of sargassum biomasses need to be taken into account when defining the uses of the biomasses or their fractions. The use of these streams outside agriculture and the food chain have been already defined, and need to be further explored and implemented.
- In Mexico, there are several commercial initiatives to produce different types of materials for construction, and polymers for applications in textiles, for example. These applications are being implemented currently by local companies.
- The content in salts and metals in sargassum biomasses opens the opportunity to use it as feedstock for nanostructured tailored materials for multiple applications. Examples are nanocarbons for use in electrodes or materials where antibacterial activity is needed. These applications are still under development at the laboratory scale.
- Programs for financial and entrepreneurship support to local parties need to be set up and continued to create the right environment for the implementation and long-term viability of the new value chains related to the sargassum uses. Where possible, new chains should be integrated with existing chains or processes.
- Since the sargassum blooms need a multidisciplinary approach to be managed successfully, collaboration between local, regional, and international stakeholders is necessary. National research programs exist already in several countries, including Mexico. Expansion of the international

collaboration needs to be supported, using the tools available, and implementing new ones, where stakeholders from different areas can get funding for innovation and knowledge exchange.

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#### Abbreviation list

- AD Anaerobic digestion
- BMP Biochemical methane potential
- VS volatile solids

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