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Harnessing *Sargassum* inundation biomass: Biobased products versus energy valorisation

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ABSTRACT

Different routes for extraction of polysaccharides (fucoidan, alginate) and biomethane production were evaluated for the valorisation of *Sargassum* spp. biomass. Modest yields of alginate (145 g/kg dry biomass) and fucoidan (43 g/kg dry biomass) were achieved through sequential low temperature acidic aqueous treatment and alkaline extraction. The crude extracts showed low molecular weights (45.2 and 79.5 kDa, respectively) and had brown colour suggesting the presence of polyphenols. High temperature aqueous treatment increased fucoidan extraction efficiency, as indicated by higher fucose content in hydrolysates; however, the extract had low molecular weight (<10 kDa) leading to low crude fucoidan yield (27 g/kg dry biomass) and low fucose content. The alginate extraction yield and composition were negatively affected by the higher temperature treatment. Anaerobic digestion (AD) tests of untreated and treated fractions of *Sargassum* biomass showed that high temperature aqueous treatment can increase the biomethane production potential by up to 5 times (from 23.5 to 153.3 m^3/ton volatile solids). The most energy-rich and AD suitable fraction from the high temperature aqueous treatment was the hydrolysate fraction, containing fucoidan and other solubilised organics, while the residual *Sargassum* biomass displayed relatively low biomethane potential (79.7 m^3/ton volatile solids). A simplified economic analysis suggests that using *Sargassum* biomass in the Caribbean can be profitable (ROI between 12 and 28 %), and products such as fucoidan and alginate may enhance economic viability. However, the study shows the sensitivity of valorisation concepts to both product prices and yields, in particular the risk associated with poor product quality.

1. Introduction

Seaweed floodings or inundations have increased in recent years in coastal areas across the globe affecting various countries in the Caribbean, Gulf of Mexico, the Atlantic Coast in the USA, western coasts of Africa and East China and Yellow Sea [1,2]. These inundations occur due to pelagic populations of seaweed, mostly *Sargassum* species, which end up affecting coastal ecosystems and communities due to their rapid decay and release of toxic gases, the additional resources required for collection and waste management, as well as the derived decrease of tourism and fishery revenues [3]. Viable valorisation routes of such seaweed floodings are thus needed to provide sustainable waste management alternatives. A wide range of potential applications have been reviewed and span agricultural products (soil application and animal feed), bioenergy, functional and bioactive ingredients and biobased plastics [4].

Sargassum species found in inundations have been reported to comprise mainly three holopelagic Sargassum morphotypes *Sargassum fluitans* var. *fluitans*, *Sargassum natans* var. *natans*, and *Sargassum natans* var. *wingei* [3,5]. However, distinct taxonomy of castings is challenging due to the presence of other biomass (e.g. seagrass) in inundations [6] and the visually similar appearance of the morphotypes [7]. Their

Abbreviations: AD, anaerobic digestion; COD, chemical oxygen demand; DW, dry weight; HPAEC, High Performance Anion Exchange Chromatography; NMR, Nuclear Magnetic Resonance; SEC-MALS, Size Exclusion Chromatography-Multi-Angle Light Scattering; VS, volatile solids; ROI, return on investment; TCI, total capital investment; TEA, techno-economic analysis; WI, whiteness index.

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biomass consists of a wide range of organic compounds such as alginate, fucoidan, laminarin, cellulose, mannitol, phenolic compounds (phlorotannins), protein and ash (minerals and metals) [5,6]. Alginate and fucoidan are in particular of great interest for seaweed valorisation as biobased products with interesting rheological and bioactive properties for growing application markets. Alginate is an anionic polysaccharide consisting of linear blocks of (1 → 4) linked β-D-mannuronate (M) and α-L-guluronate (G) units; the numbers and ratios of such units is species-dependent which inherently affects its viscosity, water binding properties and bioactivity [8]. On the other hand, fucoidan or fucans are heterogeneous polysaccharides formed by sulphated L-fucose units, with varying degrees of sulfation and other saccharide and sugar acid units [9].

Development and validation of both conventional and novel processing methods for the extraction of polysaccharides from *Sargassum* spp. biomass have gained increasing attention in recent years. For instance, Mohammed et al. [10] applied a response surface methodology for the selection of optimal conditions of alginate extraction from *Sargassum natans* using sodium carbonate and validated its rheological properties. Flórez-Fernández et al. [11] has explored ultrasound-assisted aqueous extraction to obtain alginate extracts from *Sargassum muticum* with varying molecular weight, M/G ratios and mechanical properties. Low temperature aqueous extraction of *Sargassum horneri* coupled with downstream citric acid depolymerisation and purification has shown to yield fucoidan-rich extracts with antioxidant activity suitable for applications as functional ingredient [12].

Biorefining approaches have been explored as a means to maximise the value derived from these types of biomass, either oriented to the recovery of multiple biobased products (polysaccharides and bioactive extracts [13]) or combining the recovery of biobased products with bioenergy and/or biofuels [5,14,15]. Microwave-assisted aqueous processing of *Sargassum muticum* has been shown to release fucoidan-derived oligomers and phenolic compounds while serving as pretreatment for enzymatic hydrolysis and ethanol fermentation [16]. Anaerobic digestion has been particularly identified as a platform technology for the valorisation of such biomass, where add-on biomass pretreatment and/or co-digestion with other local biogenic wastes improves conversion efficiency for biogas production and enables the use of digestates as fertiliser [4,17]. Thompson et al. [17] showed the relationship between the severity of aqueous pretreatment (120–180 °C) and the anaerobic digestibility of pelagic *Sargassum* biomass for the production of biomethane, having the potential to increase the methane production three-fold compared to untreated *Sargassum* and reducing H_2S concentration in the produced biogas. Flórez-Fernández et al. [18] proposed a biorefinery approach for *Sargassum muticum* where the production of biostimulant sap (i.e. liquid phase fraction product obtained from the washing milled fresh seaweed), fucoidan and biogas are combined. On the other hand, low temperature aqueous treatments including microwave- and sonication-assisted have been shown to have marginal effects on the anaerobic digestibility of *Sargassum* biomass sourced in the Dominican Republic [19]. Thermal conversion technologies such as pyrolysis have been explored for the production of bio-oil and biochar from *Sargassum* [20]; however, due to the inherent high moisture content of the biomass upon collection, processes such as hydrothermal processing and supercritical water gasification are deemed more suitable but have been explored to a lesser extent [4,21].

Recent literature concerning the techno-economic evaluation of *Sargassum* biomass presents compelling evidence that highlights the substantial advantages of producing biobased products in comparison to energy generation. The study by Flores-Mendoza and Lopez-Arenas [22] recently analysed four technological processing routes aimed at the production of sodium alginate, polyhydroxybutyrate (PHB), lactic acid, and bioenergy. This assessment highlighted that sodium alginate production emerges as the most promising pathway, exhibiting an impressive return on investment (ROI > 80 %) and a payback period of less than three years. Scenarios in which alginate, lactic acid, and biofertilisers are considered as co-products demonstrate improved profitability, supporting the viability of this approach. In contrast, the production of bioenergy has been identified as unfeasible due to prohibitive processing costs, highlighting a critical bottleneck within the value chain. Further research corroborates these findings and addresses critical challenges within the sector. The study conducted by Caxiano et al. [23] evaluated biorefinery configurations utilising *Sargassum muticum*, examining two distinct pathways for the residual biomass resulting from the extraction processes: anaerobic digestion to produce biogas and electricity, and an alternative route for marketing the residual seaweed solids directly as fertiliser. The results showed that the capital expenditures associated with the energy-generating scenario were 12.7 % higher than the fertiliser scenario. Notably, the biogas production scenario showed limited viability due to the low methane potential of the seaweed. At the same time, the pricing dynamics of fertiliser emerged as a decisive factor in favour of the latter scenario.

Moreover, a study by Thompson et al. [24] examined different biorefinery concepts for *Sargassum* biomass valorisation, focusing on hydrothermal pre-treatment prior to anaerobic digestion. In the mentioned study, the possibility of using organic waste as a co-feed was analysed, both with and without hydrothermal pre-treatment, and showed that co-valorisation of the residue by-product is needed to achieve economic viability.

In the present work we evaluate two valorisation routes for the utilisation of *Sargassum* biomass that combines the extraction of biobased products (polysaccharides) with biomethane production (Fig. 1). Low temperature aqueous extraction processes are integrated for the extraction of fucoidan and alginate and their compositional properties are assessed. High temperature aqueous extraction or treatment is also examined as a means to improve fucoidan extraction and its impact on alginate extraction is discussed. Finally, options for integrating high-temperature treatment with anaerobic digestion for biomethane production are examined, considering both energy recovery efficiency and the possibility of co-valorisation of biobased products. Moreover, a simplified techno-economic analysis of three concepts combining the various valorisation routes was performed to investigate the viability of these cascading approaches compared to a benchmark concept in which the biomass is used directly in the production of biogas without further treatment (Fig. 1).

2. Materials and methods

2.1. Materials

Sargassum spp. biomass was kindly provided by Climate Cleanup as part of an in-kind collaboration. The biomass was collected in Point Blanche bay in Saint Marteen between 31th of August and 15th of September 2020 from the open sea, and immediately placed on a black weed block to dry in the open air under the sun for 8 h before placing in plastic containers for transportation [25]. Before use for the present experimental work, the biomass was further dried at 60 °C to a moisture content of 2.9 % wt and milled to pass through 4 mm cutting mesh (Retsch SM300 cutter mill) and sieved to recover a fraction between 1 and 4 mm (Fig. 2). The material was stored in a sealed container at room temperature until further use. Although polysaccharide composition and properties may vary between different species of brown algae, and even among species within the same family, it was not considered practically feasible to separate *Sargassum* morphotypes prior to biomass processing and evaluation.

2.2. Extraction of fucoidan and alginate following low temperature aqueous extraction

2.2.1. Fucoidan

The extraction of fucoidan was performed according to the same methodology as previously established by Birgersson et al. [26] aimed at

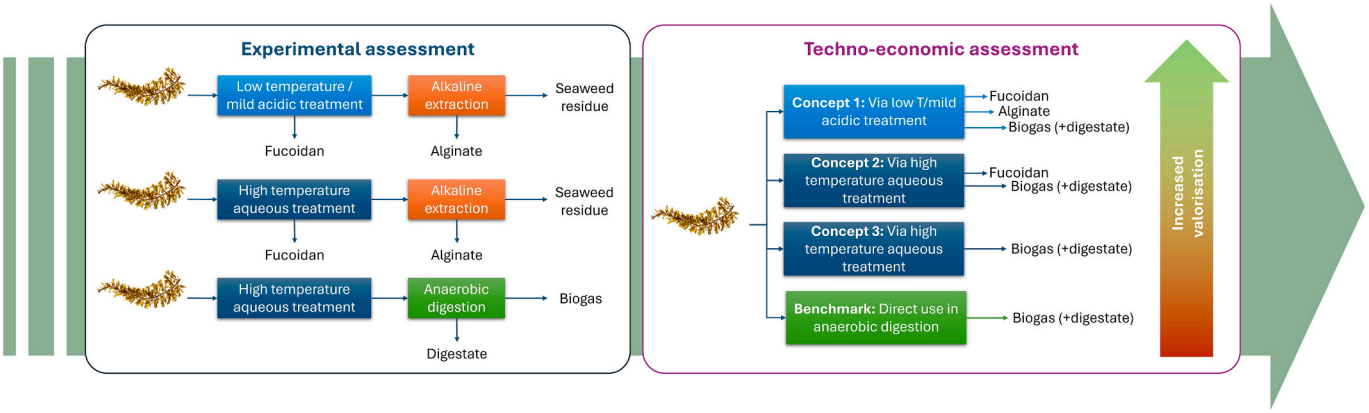

Fig. 1. Valorisation routes for the utilisation of *Sargassum* biomass.

Fig. 2. (Left) *Sargassum* spp. biomass as received; (right) *Sargassum* spp. biomass after milling and sieving to particle size between 1 and 4 mm.

co-extracting fucoidan and laminarin. Prior to treatment, 15 g of dried *Sargassum* biomass was soaked in 135 mL of water overnight. Thereafter, 225 mL of water was added to the soaked biomass, and the pH of the suspension was adjusted to 4.5 with 0.1 M HCl. The sample was incubated in a water bath at 50 °C for 3 h. The water phase was separated from the biomass, and the biomass was then mixed thoroughly with 75 mL of deionised (DI) water and again separated. The remaining solid material was reserved for alginate extraction.

The two aqueous fractions were combined and filtered using 30 μm Whatman 113 filters. To collect a potential laminarin fraction, insoluble in cold-water, the filtrate was refrigerated and then thawed in a cooling room (4 °C). After thawing, the solution was centrifuged (10,000 *g*, 15 min) to separate the precipitate from the fucoidan-rich supernatant. The precipitate was washed with cold DI water (4 °C), centrifuged again, then redissolved in 30 mL DI-water and heated at 70 °C for 2 h. Finally, the solution was filtered (2.7 μm) and lyophilized.

The fucoidan-rich supernatant was filtered (1.6 μm), transferred to dialysis tubes (3.5 kDa molecular weight cut-off or MWCO), and dialysed against 50 mM NaCl (twice) and DI-water (four times). After dialysis, the fucoidan-rich samples were neutralised and lyophilized.

2.2.2. Alginate

To extract alginates, the biomass from Section 2.2.1 was immersed in 225 mL of 0.2 M HCl and orbital shaking at 60 rpm over-night at room temperature (RT). The biomass was then washed twice with 225 mL DI-water, followed by immersion in 225 mL of 0.2 M $NaHCO_3$ (60 rpm, overnight, room temperature). The alginate-rich aqueous phase was separated from the biomass by filtration (30 μm). The residue was washed once with approximately 100 mL deionised water and combined with the initial alginate-rich filtrate. The remaining solid material was dried in an air convection oven (2 days, 60 °C).

To precipitate alginates, NaCl (0.2 % w/v) and 96 % EtOH in a 1:1 (v/v) ratio was added to the supernatant. The resulting precipitate was washed twice with 100 mL 70 % ethanol and once with 100 mL 96 % ethanol, then dried overnight at room temperature to obtain the alginate extract.

2.2.3. Characterisation alginate, fucoidan and biomass used for polysaccharide extraction (including residues)

Monosaccharide composition of the *Sargassum* biomass, final solid residue and extracts, was determined using high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD). Samples were analysed according to the protocols described by Birgersson et al. [26], and Arlov et al. [27], with methodological adaptions based on the work of Manns et al. [28]. Samples were milled in a Retsch MM 400 ball mill (10 mm steel balls, 30 mL cups, 30 Hz, 10 min) and stored in desiccator overnight. 10–50 mg of sample were transferred to 12 mL hydrolysis tubes with PTFE phenolic screw caps. Sulphuric acid (12 M, 0.5 mL) was added, and the sample was placed in a heating block at 30 °C for 60 min. DI-water was added to a final concentration of 2 M sulphuric acid and the sample was heated at 100 °C for 4 h. After cooling, 6 mL of deionised water was added to the sample, 180 μL of the solution was taken and mixed with 220 μL 1 M NaOH in a 1.5 mL eppendorf tube. The supernatant was diluted 30–60 times, filtered (0.22 μm, 13 mm syringe filter) and transferred to an HPLC vial. Monosaccharide analysis were performed on an ICS 5000+ system (Thermo Scientific) with a 4 × 250 mm CarboPac SA10 main column and 4 × 50 mm SA10 guard column. 25 μL sample was injected and eluted with a flow rate of 1.2 mL/min at 28 °C and post column addition of 0.4 M NaOH (0.3 mL/min). Each sample was injected twice, and analysed with a neutral monosaccharide method and a uronic acid method, respectively. Elution conditions and eluents for the quantification of neutral monosaccharides and uronic acids are given in SI Table 1. Factors for correcting for degradation of monosaccharides (SI Table 2) were previously determined as the ratio of peak areas for 5 mg/L standard mixtures before and after hydrolysis. For ManA and GulA, standards were prepared by hydrolyzing a pure alginate standard with a known composition (50.4 mol% GulA, determined by ^{1}H NMR [29]),

following the procedure described by Aarstad et al. [30], under the same conditions as the samples. Thus, no correction factors were required, apart from accounting for the water content (14.3 % DW, determined using an AH103 moisture analyzer from Mettler Toledo). Monosaccharide content is calculated on the basis of dry weight of sample (% dw) and it was corrected for the addition of water when glycosidic linkages are hydrolysed (anhydrous basis).

Molecular weight distributions were determined with Size-exclusion chromatography (SEC) with online multi-angle static laser light scattering (MALS). This was performed at ambient temperature on a system consisting of a solvent reservoir, isocratic pump, automatic sample injector, OHpak LB-G 6B guard and OHpak LB 806M main column. The column outlet was connected to a Dawn HELEOS-II multi-angle laser light scattering photometer (Wyatt, U.S.A.) ($\lambda_0 = 663.8$ nm) followed by a T-Rex refractive index detector (Wyatt, U.S.A). The eluent was 0.15 M $NaNO_3$, pH 6.0 with 10 mM EDTA and the flow rate was 0.5 mL/min. Samples were dissolved overnight in mobile phase (0.5 mg/mL) and filtered (pore size 0.45 μm) before injection. The injection volume was 50–100 μL. Data were collected and processed (with dn/dc = 0.150 mL/g and $A_2 = 5{\cdot}10^{-3}$ mL·mol/g^2 for alginate and dn/dc = 0.115 mL/g and $A_2 = 1{\cdot}10^{-3}$ mL·mol/g^2 for fucoidan) using the Astra (v. 7.3.21) software (Wyatt, U.S.A.).

For NMR analysis, the alginate samples were analysed according to the ASTM standard protocol F2259-10. Samples were first hydrolysed at 95 °C and pH 5.6 for 60 min, followed by an additional 50 min at pH 3.8, and then lyophilised. Fucoidans were not hydrolyzed prior to analysis. Lyophilized samples were dissolved in deuterium oxide (D_2O) (99.9 % D, Sigma-Aldrich) to a final volume of 600 μL. 3-(Trimethylsilyl)-propionic-2,2,3,3-d4 acid sodium salt (TSP) (Aldrich, Milwaukee, WI) in D_2O (1 %, 5 μL) was added for internal chemical shift reference. For alginates, TTHA (triethylenetetraminehexaacetic acid, 0.3 M in D_2O, pH 7, 20 μL) was added as a chelator to bind traces of Ca^{2+}. ^{1}H NMR spectra were recorded at 82 °C on BRUKER NEO 600 MHz equipped with 5 mm iProbe TBO. The spectra were recorded using TopSpin 3.2 or 3.5 software (Bruker BioSpin) and processed and analysed with TopSpin 4.0.7 software (Bruker BioSpin).

Nitrogen and sulphur contents of fucoidan extracts were determined using a Vario-El-Cube CHNS element analyzer (Elementar). Samples (5 mg) were placed in tin capsules in triplicate and oxidised at 1150 °C. A conversion factor of 2.5 was used to convert the S into an estimated amount of sulphite groups (-SO_3^-) in the biomass. Since no ash analysis was performed on the fucoidan fractions, S was instead converted into sodium sulphite ($SO_3^-Na^+$) by using a conversion factor of 3.2. A protein-to-nitrogen conversion factor of 5 was used for the estimation of the protein content [31].

Except for the NMR samples, which were analysed as single replicates, all other analysis were performed in triplicates.

2.2.4. Yields estimation, reproducibility and statistical analysis

All extractions were performed in triplicate and (crude) polysaccharide product yields are thus reported as the average of the three measurements. As a control, alginate was also extracted directly from soaked, untreated biomass (i.e. without prior fucoidan and laminarin extraction) in a single replicate. Monosaccharide content analyses were performed in triplicate and reported contents correspond to the average of three measurements. When more than one measurement was performed, the standard deviation of the replicates is presented.

Polysaccharide yields are presented in g/kg dry *Sargassum* biomass and were calculated as follows:

$$\text{Yield polysaccharide (g/kg)} = \text{mass polysaccharide after drying in g} / \text{mass dry } \textit{Sargassum} \text{ biomass in g} \times 1000 \quad (1)$$

When discussed, extraction efficiencies were estimated as the ratio of relevant monosaccharides and/or components representative of the polysaccharide backbone found in the polysaccharide extract to the available amount of representative components in the starting *Sargassum* biomass, as follows. The relevant monosaccharides and/or components are specified when the extraction efficiency is discussed in the text.

$$\text{Extraction efficiency (\%)} = (\text{Content of relevant components in polysaccharide extract in\%DW}) / (\text{Content of relevant components in } \textit{Sargassum} \text{ biomass in\%DW}) \times \text{Yield polysaccharide in g/kg} \times 10 \quad (2)$$

2.3. Sub-critical aqueous treatment and anaerobic digestibility tests

2.3.1. Subcritical aqueous treatment

Sargassum spp. biomass was treated in aqueous phase at two scales (2 and 20 L) in an autoclave reactor (Kiloclave, Büchi Glas Uster AG, Switzerland). For the test at 2 L scale, approx. 135 g dry *Sargassum* biomass was mixed with approx. 1.5 L demineralised water to obtain a liquid-to-solid (LS) ratio of 10 g/g dw seaweed. The mixture was stirred at 250 rpm and heated to 160 °C and maintained at this temperature for 1 h. After the test, the slurry was centrifuged (2740 *g*, 15 min, Thermo Scientific, SL 40R) to separate the hydrotreated solids from the fucoidan-containing hydrolysate. Sub-samples of the hydrotreated solids and hydrolysate were taken for evaluating the recovery of fucoidan and alginate. The remainder of the samples were either dried at 60 °C in an air-ventilated oven or stored frozen until further analyses.

At 20 L scale, approx. 760 g dry biomass was mixed with 15 L demineralised water to obtain a liquid-to-solid (LS) ratio of 20 g/g dw seaweed. The mixture was stirred at 500 rpm and heated to 160 °C and maintained at this temperature for 0.5 h. The pH at the start of the test was 6.2 and decreased to 5.3 after the test. After treatment, the reactor was allowed to cool down. A subsample of the slurry was kept apart for anaerobic digestion testing, while the remaining slurry was filtered (Whatman GF/D, 2.7 μm) under vacuum. The hydrotreated solids were dried at 60 °C in an air-ventilated oven until constant weight. The filtrate or hydrolysate was stored frozen at −18 °C until further analyses.

2.3.2. Fucoidan and alginate recovery from high severity aqueous treatment

The hydrolysate obtained from the 2 L scale test was filtered under vacuum (Whatman GF/D, 2.7 μm) before further purification of fucoidan following an adapted protocol [32]. Namely, the hydrolysate was dialysed using 10 kDa MWCO dialysis flasks (Slike-A-Lyzer™ dialysis flask, Thermo Scientific) for 24 h replacing the demineralised water two times during the first 6 h. Later, the dialysed hydrolysate was combined with 1 volume part of 1 % $CaCl_2$ solution and stored overnight at 4 °C. After this, the mixture was centrifuged at 2740 *g* for 15 min (Thermo Scientific, SL 40R). The supernatant recovered was further mixed with 2 volume parts of ethanol and stored overnight at 4 °C. The product mixture was centrifuged at 2740 *g* for 15 min (Thermo Scientific, SL 40R) and the supernatant discarded to recover a crude fucoidan pellet that was freeze-dried to constant weight.

To evaluate the potential recovery of alginate from *Sargassum* treated at high temperature, the wet treated solids obtained at 2 L scale were treated through alkaline extraction using 0.35 M Na_2CO_3 at 80 °C, 6 h (10 g/g dw solids). From this test, an alkaline extract and a final seaweed residue were also recovered. The pH of the alkaline extract was adjusted to 2 with hydrochloric acid to precipitate sodium alginate. The sodium alginate was separated with a metal mesh filter and washed with demineralised water. The precipitate was redissolved in demineralised water with a liquid-to-solid ratio of 10 g/g precipitate and neutralised with NaOH. The neutralised solution was mixed with 1 volume part of ethanol containing 0.2 % wt NaCl to re-precipitate the alginate. The alginate was recovered as a pellet through centrifugation at 2740 *g* for 15 min (Thermo Scientific, SL 40R). The alginate pellet was further

washed with ethanol, re-centrifuged and the final pellet freeze-dried to constant weight.

2.3.3. Biomethane potential

Biomethane potential (BMP) tests were performed to characterise the digestibility of *Sargassum* biomass before and after hydrotreatment, as well as of the separated hydrotreated solids and hydrolysate. For these tests, the samples obtained from the high temperature aqueous treatment test at 20 L scale were mixed with active inoculum from an anaerobic digester previously degassed following the standard method VDI 4630:2016 for the characterisation of fermentation of organic materials. Anaerobic digestion tests were performed with an inoculum to substrate ratio on volatile solid basis of 4 to 1 and a digester volume to headspace ratio of 7 to 3 at 37 °C for 40 days. Biogas was sampled in bags and analysed using a portable analyzer (Biogas5000, GeoTech). Volatile solids (VS) were determined as the organic fraction of the dry solids of samples through incineration of the sample at 550 °C (EN 14775:2009).

2.3.4. Characterisation of products from high temperature aqueous treatment

Moisture content in solid samples or total solids content in hydrolysate was measured gravimetrically by drying at 105 °C in an air-ventilated oven to a constant weight. Ash content was determined gravimetrically by treating the samples at 550 °C for 12 h. The mineral elemental composition was measured following inductively coupled plasma atomic emission spectroscopy ICP-AES (Thermo ICAP 6000). For this analysis, samples were digested using HNO_3 before analysis. Elemental carbon, hydrogen and nitrogen (CHN) content was determined in a CHNS/O organic elemental analyzer (FLASH 2000, Thermo Fisher Scientific). The analysis was performed according to the NEN-EN-ISO 16948 Solid biofuels standard.

For this part of the work, saccharide content in solid samples was determined via an acid hydrolysis protocol adapted for brown seaweed *Saccharina latissima* [33]. Briefly, 300 mg of dry solid sample was treated with 3 mL 72 % w/w H_2SO_4 at 30 °C for 60 min. After this, deionised water was added to the sample to a final volume of 30 mL and allowed to incubate at 99.5 °C for 3 h. The liquid fraction was further separated by centrifugation and analysed via HPAEC-PAD to quantify the concentration of monosaccharides (galactose, glucose, xylose, fucose, rhamnose), sugar alcohols (glycerol, mannitol) and uronic acids (galacturonic, guluronic, glucuronic, mannuronic and iduronic acids). For this, an ICS-6000 HPIC system (Thermo Scientific Dionex) was used consisting of a CarboPac PA1 main and guard column. A gradient of NaOH and sodium acetate was used as eluent with a flow of 0.25 mL/min (SI Table 3). Samples were neutralised with barium carbonate before injection, fructose was used as internal standard and calibrations were made with model compounds. Monosaccharide content is calculated on the basis of dry weight of sample (% dw) and it was corrected for the addition of water when glycosidic linkages are hydrolysed (anhydrous basis).

2.3.5. Yields estimation, reproducibility and statistical analysis

At the scales used for sub-critical aqueous treatment, extractions were performed in single replicates. Monosaccharide content analyses were performed in duplicates and reported contents correspond to the average of two measurements. When more than one measurement was performed, the standard deviation of the replicates is presented. Polysaccharide yields and extraction efficiencies were calculated as described in Eqs. (1) and (2), respectively.

2.4. Techno-economic analysis

Three scenarios for *Sargassum* biomass valorisation were included in a simplified techno-economic analysis (Fig. 1): Concept 1, alginate, fucoidan and biogas co-production, enabled through low-temperature aqueous treatment; Concept 2, fucoidan and biogas co-production enabled through high temperature aqueous treatment; Concept 3, biogas production only enabled through high temperature aqueous treatment. A scenario in which *Sargassum* biomass was directly used as feedstock for anaerobic digestion without further treatment was used as benchmark. Each scenario was evaluated using an input capacity of 4000 t of dried biomass per year, operating for 8000 h annually over a ten-year lifespan. This capacity aligns with similar techno-economic studies that identify it as the minimum amount of feedstock necessary for industrial applications [20]. The system boundaries considered in this analysis encompass the processing of dried raw material through to the utilisation of the final products. The main assumptions for the economic assessment are presented in SI Table 9.

The process yields were derived from experimental data obtained in this study. Vendor information, engineering principles, and relevant techno-economic analyses of comparable processes informed the selection of equipment and considerations for scale-up. Capital costs and operating expenditures were derived from peer-reviewed studies, industrial cost reports, as outlined in SI Table 10. The costs of raw materials, waste disposal, and products are reported in Table 1. The cost of equipment obtained from literature conceptual equipment cost sourced from literature and was adjusted to the plant construction year (2023). The size of the equipment was scaled up to meet the specifications using Eqs. (1) and (2), respectively, where n is the scaling factor (0.6), and CEPCI is the chemical engineering plant cost index [34].

$$\text{Scaled}-\text{up cost} = \text{Original cost} \times (\text{Scaled}-\text{up capacity}/\text{Original capacity})^{n} \quad (3)$$

$$\text{Cost in 2023} = \text{Original cost} \times (\text{CEPCI}_{2023}/\text{CEPCI}_{\text{base}}) \quad (4)$$

A detailed breakdown of the equipment associated with each process section across Concepts 1 to 3 (Fig. 1) and the benchmark is provided in SI Tables 11–14 and SI Figs. 4–7. Economic performance was assessed using the return on investment (ROI), which is defined in this context as the ratio of pre-tax cash flow to total capital investment (TCI). Economic calculations were conducted using Microsoft Excel® software.

3. Results and discussion

3.1. Sargassum biomass composition

The initial alginate content was determined to be 20.7 % DW based on total uronic acid content (Table 2). This level was considerably higher than those reported in a previous study assessing the composition of *Sargassum* spp. collected from various locations in the Caribbean, which found alginate contents ranging from 5 to 16 % DW [41]. However, it was still lower than the levels typically found in the main commercial alginate-producing species – *Laminaria hyperborea*, *Macrocystis pyrifiera* and *Saccharina japonica* – which generally contain between 22 and 40 % DW alginate, depending on factors such as species,

Table 1
Prices used in the analysis for the raw materials, waste disposal and products.

Category	Item	Price	Unit	Reference/source
Raw materials	Sargassum	0.05	€/kg	Collection and drying expenses
	Process water	0.00053	€/kg	[35]
	HCl	0.23	€/kg	[36]
	$NaHCO_3$	0.53	€/kg	[37]
Waste disposal	Wastewater	1	€/m^3	[38]
Products	Biogas	50	€/MWh	[39]
	Fucoidan	30	€/kg	[40]
	Alginate	8	€/kg	[23]
	Digestate	0.2	€/kg	[24]

Table 2
Composition of *Sargassum* spp. biomass used in the present study.

	Content in dry weight basis
Ash	36.4 ± 0.1
Mannitol	6.0 ± 0.2
Fucose	3.1 ± 0.1
Galactose	0.9 ± 0
Glucose	5.7 ± 0.3
Xylose	0.6 ± 0
Mannose	1.0 ± 0
Guluronic acid	11.6 ± 0.5
Glucuronic acid	3.4 ± 0.1
Mannuronic acid	9.1 ± 0.4
-SO_3[a]	5.1
Protein	3.8 ± 0.07
Unidentified fraction	18.4

[a] Based on total sulphur content.

seasonal variations and harvesting location [42–45].

Similarly, the mannitol content observed in the *Sargassum* spp. biomass was substantially lower compared to levels reported in other species, including *Laminaria hyperborea*, *Saccharina latissima* and *Alaria esculenta* (all belonging to the order Laminariales) which have reported levels that vary between 10 and 25 % DW during the growing season [42]. The fucose content was within the range reported previously for *Fucus* spp. and *Ascophyllum nodossum* (1–3 % DW) [46]. The ash content observed in the biomass was also high (37.5 % DW) despite the absence of sand, with potassium, sodium, calcium and magnesium as the most abundant metals found in the inorganic fraction (SI Table 8). Cellulose content in different brown algae species can vary greatly, reportedly ranging from as low as 2.2 % DW in *Spatoglossum asperum* [47] to as high as 14 % DW in *Saccharina latissima* and *Laminaria digitata* [42]. The glucose content of the *Sargassum* spp. was 5.7 % DW. As it is later discussed in Section 3.2, only traces of laminarin were observed; thus, nearly all glucose is expected to originate from cellulose.

3.2. Extraction of fucoidan and alginate fractions from Sargassum biomass following low temperature aqueous extraction

To evaluate the potential use of the collected *Sargassum* spp. biomass for biopolymer production, specifically high-value polysaccharides, the biomass was treated according to a recently developed protocol by Birgersson et al. [26] for the sequential extraction of fucoidan, laminarin and alginate. Both alginates and fucoidans are prone to degradation under conditions of low pH and high temperatures [48–50]. To minimise structural modification of native fucoidans, such as loss of sulphate groups and depolymerisation, while still allowing for subsequent extraction of high molecular weight alginates, the simultaneous fucoidan-laminarin extraction employs only mildly acidic conditions and moderate heat (pH 4.5, 50 °C, 3 h) [26]. The process yielded three crude polysaccharide fractions, namely referred to as alginate, laminarin and fucoidan, each of which was assessed individually. Additionally, the composition of the remaining residue was analysed to assess its potential for cellulose extraction.

The yields and chemical composition of the extracted fractions are reported in Table 3. The crude alginate yield was 145 g/kg, corresponding to an extraction efficiency of 43.1 % of the initial mannuronic and guluronic acids in the raw biomass (Table 3). The yield of the crude fucoidan fraction was 43 g/kg. However, when analysing the chemical composition, it was noted that over 50 % DW of this product comprised of alginate. Fucoidans from the family *Sargassum* have previously been reported to consist of heterofucans, with diverse monosaccharide composition where the molar concentration of fucose ranges from 10 to 90 mol-% of total monosaccharides, depending on several factors such as species, extraction conditions and type of purification [51]. The total weight percent of fucose, arabinose, galactose, rhamnose, xylose and glucuronic acid, was therefore added together with the sulphate groups

Table 3
Yields (g/kg dry weight *Sargassum* biomass), dry weight monosaccharide composition, nitrogen content, and sulphate content (determined as sodium sulphite, -$SO_3^-Na^+$) of crude fucoidan, alginate and residual biomass from moderate acidic conditions.

	Crude polysaccharide fractions		Residual biomass
	Alginate	Fucoidan	
Yield (g/kg)	**145 ± 3**	**43 ± 1**	**407 ± 12**
Mannitol (% DW)	0 ± 0	0.3 ± 0	0.3 ± 0
Fucose (% DW)	1.1 ± 0	4.9 ± 0.1	4.8 ± 0.1
Galactose (% DW)	0.2 ± 0	2.0 ± 0	1.3 ± 0
Glucose (% DW)	0.1 ± 0	0.8 ± 0	11.2 ± 0.3
Xylose (% DW)	0.3 ± 0	1.4 ± 0	0.8 ± 0
Mannose (% DW)	0.6 ± 0	2.9 ± 0.1	1.5 ± 0.1
Arabinose (% DW)	0 ± 0	0.1 ± 0	0 ± 0
Rhamnose (% DW)	0 ± 0	0.3 ± 0	0.1 ± 0
Guluronic acid (% DW)	35.5 ± 0.3	23.8 ± 0.3	9.0 ± 0.1
Glucuronic acid (% DW)	1.2 ± 0	4.4 ± 0.2	5.5 ± 0.1
Mannuronic acid (% DW)	26.0 ± 0.2	31.1 ± 0.7	5.7 ± 0.1
-SO_3Na (% DW)	0.8 ± 0	4.9 ± 0.1	3.3 ± 0.8
Nitrogen (% DW)	0 ± 0	0.3 ± 0	0.8 ± 0.1
Unidentified fraction (% DW)	33.1	22.8	55.7

to determine the actual yield of fucoidan present in the fraction. Together these accounted for 25.6 % DW of the crude fucoidan, resulting in an actual yield of 18 g fucoidan/kg biomass, and an extraction efficiency of 6.8 % based on the fucose content in the raw biomass. The 'Unidentified fraction' remaining after summing the analysed components shown in Table 3 expectedly consists of varying concentrations of ash [26], pigments (including polyphenols) and proteins, as indicated by the nitrogen content [52].

The content of laminarin in brown algae varies greatly depending on seasonal fluctuations and species [42]. The method used to extract fucoidan, was expected to also extract potential laminarin. However, as shown in SI Table 4, the collected precipitate (presumed to be laminarin) yielded only 6 g/kg of *Sargassum* biomass and contained mere trace amounts of glucose (1.69 % DW). Furthermore, there was no substantial amount of glucose detected in the fucoidan fraction, which would have contained unprecipitated laminarin. Hence, the results indicate that the biomass processed in this study did not contain laminarin.

The residual biomass contained 11.2 % DW glucose, assumed to originate exclusively from cellulose. This corresponds to 45.6 g of cellulose per kg *Sargassum* biomass processed, accounting for 80 % of the estimated glucose present in the raw biomass.

The alginate and fucoidan were further characterised by SEC-MALS and NMR to gain insights into their structural composition, molecular weights, and molecular weight distribution (Table 4, SI Fig. 1). The M_w of alginate fraction was 45 kDa, which was considerably higher than previously reported values of alginates extracted from other *S. muticum* collected in the Caribbean (3.2 kDa [10]), but slightly lower than alginates extracted from *S. muticum* harvested outside the coast of Morocco (76 kDa [53]). Both studies applied higher temperatures (80 °C) during the alkaline treatment, but shorter incubation time (3 h or 6 h), possibly explaining the higher crude yields obtained, 21.7 % and 23 % DW, respectively [10,53].

Alginate is the brown algae-derived polysaccharide with the highest

Table 4
The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) together with the polydispersity index (PDI = M_w/M_n) of alginate and fucoidan.

	M_n (kDa)	M_w (kDa)	PDI (M_w/M_n)
Fucoidan	19.2 ± 1.3	79.5 ± 2.8	4.1 ± 0.2
Alginate	25.3 ± 0.7	45.2 ± 0.6	1.8 ± 0.0

commercial value, used in a range of industrial applications, primarily for its thickening properties and ability to form hydrogels with divalent cations, such as Ca^{2+}. The molecular weight and co-monomer distribution are key functional attributes which influence their physical and mechanical properties. The distribution of guluronic (G) and mannuronic (M) groups is of particular importance, since the average length of G-blocks has a profound effect on the strength and elasticity of the alginate hydrogels [54,55]. Table 5 presents the distribution of M, G, and their diads and triads in the recovered alginate. The extracted alginates had a high G content (F_G = 0.64), consistent with values commonly reported for alginates from species in the genus *Sargassum* [56], and comparable to high quality alginates extracted from the stipes of *Laminaria hyperborea*, typically having F_G of 0.60 to 0.70 [43,56]. However, no other similarities are shared with the alginates reported from *Laminaria hyperborea*, with a reported M_w around 600 kDa [56]. When processed, most commercial alginates have molecular weights around 200 kDa [55], considerably higher than the molecular weights observed in this study (Table 4). Just like the fraction of G, the molecular weights are important for gel strength and elasticity, and low molecular weights results in poor thickening properties [55].

As illustrated in Fig. 3A, the *Sargassum* alginate had a deep brown colour, even after several rounds of washing with ethanol, indicating that the samples contained high concentrations of co-extracted polyphenols [50], tightly associated or covalently bound to the alginate. The final colour of the extracted alginates is important for its end-use applications, as brown is generally considered aesthetically undesirable [10]. Traditionally, formalin (diluted formaldehyde) has been used as a pre-treatment of brown seaweeds in the alginate industry, serving both as a preservative by inhibiting microbial growth and decomposition and as a cross-linking agent for polyphenols, thereby preventing discoloration of the alginates [56]. However, as shown in Fig. 3B, alginates extracted from other species, here *Saccharina latissima*, might exhibit an appreciable whiter appearance than the *Sargassum* alginate, even when the formalin treatment is not implemented.

Due to the potential allergenic and carcinogenic effects in humans, the European Union is restricting the use of formalin and it is expected that formalin will eventually be phased out [56]. However, as noted by Mohammed et al. [10], alginates extracted from Caribbean *Sargassum natans* remained brown in colour even when a formalin pretreatment was applied. Also after inclusion of a bleaching step using hydrogen peroxide (negatively affecting the viscosity and M/G ratio), the alginate still had a lower whiteness index (WI) compared to a commercial "food grade" alginate (WI = 76 and 89, for bleached *Sargassum natans* alginate and food grade alginate, respectively). Furthermore, it is possible that the high polyphenol content in the *Sargassum* spp. alginates is at least partly responsible for the low molecular weight observed. Alginate chains are susceptible to oxidative-reductive depolymerization in the presence of free radicals, such as hydroxy radical species generated by polyphenols. These reactive species can rapidly reduce the degree of polymerisation in alginates [50,55].

However, while the alginate quality may be poorer than from species traditionally used for extraction of high-quality alginates (including species from *Laminaria*, *Lessonia* and *Ecklonia*), the Caribbean *Sargassum* species offer the advantage of being an abundant, unwanted resource that is generally considered waste material. Consequently, the extracted alginates hold potential for low-value applications, particularly if issues related to discoloration from co-extracted polyphenols during processing can be mitigated, for example, through improved biomass handling during harvesting. Machado et al. [41] showed that the drying method employed to stabilise the *Sargassum* can influence its biomass composition. In particular, their study highlighted how sun drying may result in higher proportion of polyphenolics and lower alginate contents compared to freeze drying. The *Sargassum* biomass used in the present study was collected from open sea and sun-dried which may have promoted the aforementioned features. It is also worth noting that, for reference, an additional alginate extraction was performed, without the preceding fucoidan extraction. The properties (M_w, M/G distribution, and colour) of the alginates were almost identical, but the yield was slightly higher, reaching 190 g/kg (SI Tables 6 and 7). This shows that the sequential treatment, with the acidic treatment prior to alginate extraction, only had a minor on impact on the quality and recovery of the alginate fraction.

The M_w of the crude fucoidan fraction was determined to be 79.5 kDa, while the M_n was 19.2 kDa, resulting in a polydispersity index (PDI) of 4.1 (Table 4). NMR analysis of the fucoidan (SI Fig. 1) indicated that the co-extracted alginate present in the fucoidan fraction was of low molecular weight, likely having a degree of polymerisation below 50 (>10 kDa). Thus, it is likely that the alginates contributed to the low M_n, resulting in a high PDI. Fucoidans from *S. muticum*, *S. natans* and *S. fluitans* have previously been reported with molecular weights in the range of 25–50 kDa [57], 50–135 kDa [58] and 60 kDa [59], respectively. Compared to fucoidans from many other species of brown algae, often ranging from 100 kDa up to well over 1000 kDa [46,60,61], the molecular weights reported for these *Sargassum* species appear consistently low. In addition, compositional data reported in Table 3 was used to calculate the degree of sulphation (DS) of the fucoidan, which was determined to be 0.42 sulphate units per monosaccharide unit. This estimation excluded glucose, mannitol, mannuronic acid, and guluronic acid, which likely originate from co-extracted laminarin and alginate rather than being inherent structural units of the polymer [51,52]. Highly sulphated fucoidans can exhibit DS values of up to 1.7 [62]. Lastly, just like the *Sargassum* alginate, the fucoidan fraction was also brown, although with a lighter shade (Fig. 3C), indicating the presence of co-extracted polyphenols [52].

For a more detailed assessment of the structural and compositional characteristics of the extracted fucoidan (e.g. by NMR spectroscopy, SEC-MALS or linkage analysis), additional purification steps are required, such as ion-exchange and/or carbon filtration [61,62]. Purification is also necessary when aiming to evaluate the biological properties of fucoidan. However, numerous studies indicate that fucoidans with high fucose and sulphate content generally exhibit stronger biological activity than those with a more diverse sugar composition and lower degrees of sulphation [51,61,62]. The latter is the case with the fucoidan obtained in this study, which displayed a comparatively low degree of sulphation and high heterogeneity.

3.3. High temperature aqueous treatment of Sargassum biomass and impact on fucoidan and alginate

Temperatures above 70 °C have been found to promote the extraction of fucoidan from brown seaweeds in the absence of acid catalysts or additives [32,63,64]. A high temperature aqueous extraction was applied at 160 °C to the *Sargassum* biomass to assess the impact of such conditions on the extraction of fucoidan and alginate. The selection of the experimental conditions was based on prior unpublished work by the authors with *Alaria esculenta* (SI Fig. 2) and the work reported elsewhere [32]. Getachew et al. [32] explored the impact of a wide range of temperatures (120–200 °C) in aqueous extraction of *Fucus vesiculosus*

Table 5
Fractions (F) of mannuronic acid (M) and guluronic acid (G) residues and the distribution of their diads and triads, together with the average length of the G-blocks (NG > 1) in the alginate as determined via NMR spectroscopy.

	F_G	F_M	F_{GG}	$F_{GM,MG}$	F_{MM}	$F_{GGM,MGG}$	F_{MGM}	F_{GGG}	$N_{G>1}$
Alginate	0.64	0.36	0.56	0.08	0.28	0.03	0.04	0.53	17

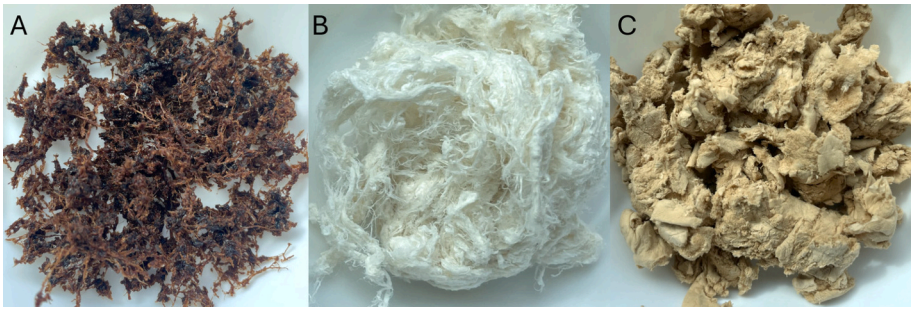

Fig. 3. (A) Photograph of the alginate extracted from the *Sargassum* biomass in this study, exhibiting a deep brown colour. (B) Alginate extracted from *Saccharina latissima* using the same extraction procedure as employed in this study, showing an almost white colour (included for visual comparison only) (C) Fucoidan extracted from *Sargassum* biomass, displaying a light brown colour. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 6
Yields (g/kg dry weight *Sargassum* biomass), dry weight monosaccharide composition, nitrogen content and sulphate content (determined as sodium sulphite, -SO_3Na) of crude fucoidan, alginate and residual biomass from high temperature aqueous treatment (2 L scale).

	Hydrolysate[a]	Crude fucoidan	Crude alginate	Residual biomass
Yield (g/kg)	**281.9**	**27.6**	**24.0**	**421.1**
Mannitol (% DW)	14.6 ± 0.2	0 ± 0	0	0 ± 0
Fucose (% DW)	5.8 ± 0.03	3.7 ± 0.03	0	0 ± 0
Galactose (% DW)	1.7 ± 0.1	12.5 ± 0.05	0	0 ± 0
Glucose (% DW)	0.5 ± 0.01	2.7 ± 0.00	0	14.9 ± 0.5
Xylose (% DW)	2.1 ± 0.00	5.7 ± 0.03	0	0 ± 0
Mannose (% DW)	0 ± 0	0 ± 0	0	0 ± 0
Arabinose (% DW)	0 ± 0	0 ± 0	0	0 ± 0
Rhamnose (% DW)	0 ± 0	0 ± 0	0	0 ± 0
Guluronic acid (% DW)	0.1 ± 0.2	3.9 ± 0.00	17.55	0 ± 0
Glucuronic acid (% DW)	1.5 ± 0.1	0 ± 0	0	0 ± 0
Mannuronic acid (% DW)	0 ± 0	2.4 ± 0.01	2.98	0 ± 0
-SO_3Na (% DW)	[b]	[b]	[b]	[b]
Nitrogen (% DW)	[b]	[b]	[b]	[b]
Ash (% DW)	59.1	23.8 ± 0.3	24.31	10.0 ± 0.1
Unidentified fraction (% DW)	13.91	45.40	55.17	75.1

[a] Hydrolysate after filtration and prior to dialysis and freeze-drying, normalised by the total solids content.
[b] Not measured.

and found that the fucoidan extraction yield was maximised at 160 °C. After the aqueous extraction, the hydrolysate was refined to recover the crude fucoidan fraction through filtration, dialysis (>10 kDa) and freeze-drying. Alginate was further extracted and refined from the residual biomass after the high temperature aqueous extraction. Table 6 presents the yields and chemical composition of the extracted fractions. The yield of the crude fucoidan fraction was 27 g/kg which was lower than that obtained through the low temperature aqueous extraction. The total saccharide content of this fraction was low (30.8 % DW) and a low content of fucose was observed. Taking the chemical composition into account, an extraction efficiency of 3.2 % based on the fucose content of the *Sargassum* biomass was estimated. However, the extraction efficiency was 53 % when taking into account the fucose content of the hydrolysate prior to the recovery of the crude fucoidan fraction. This indicates that the molecular weight of the fucoidan was lower than 10 kDa, leading to a significant loss during dialysis.

While the high temperature treatment can lead to a decrease in molecular weight due to autohydrolysis of the polysaccharides, prior work has shown that high molecular weight fractions can still be obtained under such conditions. Saravana et al. [64] observed that highest yields of crude fucoidan from *Saccharina japonica* were obtained at 127 °C for a residence time of 12 min based on the initial weight of the seaweed. Under such conditions, the crude fucoidan had similar monosaccharide composition and slightly lower molecular weight than when extracted under low temperature conditions (25 °C, 2 h, 0.05 M HCl). Álvarez-Viñas et al. [65] fractionated fucoidan extracted from *Sargassum muticum* through aqueous treatment at 170 °C and observed that approx. 70 % of the extract was recovered through membrane filtration at cut-offs higher than 10 kDa. Balboa et al. [66] only observed an increase of fucoidan fractions with molecular weight lower than 12 kDa when extracting *Sargassum muticum* through aqueous treatment at 190 °C or higher temperatures. Other research, using pre-refined fucoidan from *Fucus vesiculosus*, have shown that treatments at 120 °C for up to 90 min decrease the molecular weight of fucoidan from 38 kDa to approx. 10 kDa [67].

Variability in the measured molecular weight distributions of extracted fucoidans can be well related to the original properties of the native polysaccharide matrix of the seaweed. For instance, the rate of hydrolytic cleavage of fucans have been shown to be affected by their sulphation pattern [49]. However, further research on the characterisation of native fucoidans and their hydrolysis kinetics is still needed.

Considerably high amounts of galactose, glucose and xylose were observed in the crude fucoidan fraction, accounting for 20 % DW of the fraction. This suggests that more limited degradation of these polysaccharide fractions occurred during the thermal treatment. Furthermore, guluronic and mannuronic acid were found in relatively lower concentrations (6.3 % DW) in the crude fucoidan fraction compared to the crude fucoidan extract recovered from the low temperature aqueous extraction or the high temperature hydrolysate before recovery of the crude fucoidan fraction.

Alginate after the high temperature treatment was recovered in a low yield (24 g/kg) compared to the alginate recovered after the low severity extraction. The alginate only contained 20.5 % DW uronic acids, with a molar ratio of guluronic to mannuronic acid of 6 to 1. This ratio was significantly higher than observed in the alginate recovered from the *Sargassum* biomass after low temperature aqueous treatment. A large fraction of the recovered alginate was not identified in the chemical characterisation. This was a clear indication of extensive degradation of the alginate in the *Sargassum* biomass under the high temperature aqueous extraction.

After high temperature aqueous extraction and alginate recovery, the residual biomass contained 14.9 % DW glucose, which accounted for 110 % of the estimated glucose present in the initial biomass, suggesting that the glucose content in the raw biomass could have been underestimated. However, extensive degradation of the residual biomass occurred since the unidentified fraction corresponded to 75 % DW and no other saccharides were observed in the residual material.

Prior work has shown the suitability of aqueous treatment without acids for the promotion of the extraction of fucoidan from brown

seaweeds [32,64–66]. However, the present work shows the negative impact that the severity has on the alginate fractions in the *Sargassum* biomass. This in addition to the evidence of the extensive decrease of molecular weight of the fucoidan in the hydrolysate shows that high temperature aqueous treatment may have limited suitability for *Sargassum* biomass valorisation routes in which polymer applications with rheological and bioactive properties is intended. High temperature aqueous treatment could potentially be implemented when the objective is to recover low MW fractions of fucoidan for applications in which these fractions display suitable bioactivity [48,67].

3.4. Biomethane potential via high temperature aqueous treatment

Aqueous treatment has been shown to promote digestibility of *Sargassum* biomass and could provide opportunities for a cascading processing approach for the co-production of high-value compounds and bioenergy [4,17,18]. To explore this, a high temperature aqueous treatment test was performed at a larger scale (20 L) with the *Sargassum* biomass to produce sufficient amounts for anaerobic digestion (AD) tests. Table 7 shows the yields and composition of the hydrolysate and residual biomass from *Sargassum* from this treatment. The saccharide content of the hydrolysate obtained at 20 L scale was lower than that obtained at 2 L, with a total saccharide concentration of 19.0 % DW compared to 26.4 % DW. The fucoidan extraction efficiency at this scale was estimated as 77 % based on the fucose content in the hydrolysate and initial *Sargassum* biomass, higher than observed at smaller scale. A sub-sample of the hydrolysate was dialysed to retain fractions with MW higher than 10 kDa. This sample showed higher fucose retention than the hydrolysate from the smaller scale experiment, with a fucose content of 11.5 % DW, corresponding to an extraction efficiency of 30 %, indicating that the hydrolysate contained a higher fraction of high MW fucoidan. This variability in the hydrolysates from the two tests at 2 L and 20 L scales was attributed to differences in terms of operational conditions. On the one hand, a higher LS ratio and shorter residence time were applied at the larger scale compared to the smaller scale test. However, unintended differences regarding mass and heat transfer phenomena could be expected due to differences in the geometry of the autoclave vessels at the two scales, the applied mixing rates as well as the heating profiles (e.g. longer heating time required at larger scale). However, inconsistent with the higher fucose extraction yield, uronic acids were not detected in the upscaled hydrolysate, which may be related to the high thermal degradability of these compounds [68].

Table 7
Yields (g/kg dry weight *Sargassum* biomass), dry weight monosaccharide composition, nitrogen content and sulphate content (determined as sodium sulphite, -$SO_3^-Na^+$) of hydrolysate and residual biomass from high temperature aqueous treatment (20 L scale).

	Hydrolysate[a]	Dialysed hydrolysate	Residual biomass
Yield (g/kg)	**507.1**	**80.8**	**385.1**
Mannitol (% DW)	11.5 ± 0.08	5.8 ± 0.04	1.27 ± 0.02
Fucose (% DW)	4.7 ± 0.01	11.5 ± 0.06	0.64
Galactose (% DW)	1.28 ± 0.01	6.8 ± 0.08	0.37 ± 0.01
Glucose (% DW)	0.37 ± 0.01	1.7 ± 0.15	12.2 ± 0.2
Xylose (% DW)	0.76 ± 0.00	2.5 ± 0.02	0 ± 0
Mannose (% DW)	0.64 ± 0.01	2.8 ± 0.01	0 ± 0
Arabinose (% DW)	0 ± 0	0 ± 0	0 ± 0
Rhamnose (% DW)	0 ± 0	0 ± 0	0 ± 0
Guluronic acid (% DW)	0 ± 0	0 ± 0	1.76 ± 0.14
Glucuronic acid (% DW)	0 ± 0	0 ± 0	0 ± 0
Mannuronic acid (% DW)	0 ± 0	0 ± 0	0 ± 0
-$SO_3^-Na^+$ (% DW)	10.3	[b]	1.69
Nitrogen (% DW)	0.56 ± 0.00	[b]	1.18 ± 0.04
Ash (% DW)	57.8 ± 0.2	29.9 ± 2.7	15.5 ± 0.1
Unidentified fraction (% DW)	12.1	39.0	65.39

[a] Hydrolysate after filtration of the treated slurry, yield based on total solids content and composition normalised by the total solids content to be presented in dry weight basis.
[b] Not measured.

The most abundant saccharide in the residual biomass was glucose (12.2 % DW), with some minor amounts of mannitol, fucose, galactose and guluronic acid. Glucose recovery accounted for 82 % based on the initial available amount of glucose in the *Sargassum* biomass. Similar to the smaller scale test, the residual biomass contained a large fraction of unidentified components (65 % DW), indicating significant degradation of the biomass matrix under the treatment conditions.

AD tests were performed on untreated *Sargassum* biomass, and treated fractions in three different ways: (1) treated slurry without solid-liquid separation, (2) separated treated wet solids, and (3) hydrolysate. The latter was with the objective to identify a baseline of promotion of digestibility of the *Sargassum* and the suitability of either fraction (residual biomass and hydrolysate) for biomethane production. Fig. 4 shows the cumulative biogas formation during anaerobic digestion of the different samples. The untreated *Sargassum* biomass displayed a lag phase of 8 days before biogas was released, and produced the lowest total amount of biogas from all tests after 40 days (45 L/kg volatile solids or VS). The treated slurry and hydrolysate showed almost immediate digestibility with biogas release within 1 day. The residual biomass had better digestibility than the starting *Sargassum* biomass; however, the biogas formation rate and cumulative production were lower (127 L/kg VS by 40 days) than from the treated slurry and hydrolysate (230 and 254 L/kg VS, respectively).

Table 8 presents digestibility properties of the *Sargassum* biomass and treated fractions. VS content of the treated slurry and hydrolysate were lower than in the starting *Sargassum* biomass; while the residual biomass showed significantly higher VS. On the other hand, chemical oxygen demand (COD) increased substantially from 150 mg/g dry matter in the initial biomass to 1259 mg/g dry matter in the treated slurry. Contrary to the measured VS content, the residual biomass had lower COD than the hydrolysate. These observations are consistent with the biogas release rate and cumulative yields observed for the samples. A higher COD is an indication of higher energy content in the context of biogas production. Furthermore, it is observed that the digestibility of the hydrolysate fraction was higher than that of the residual biomass, since the former had a biomethane potential at 28 days two times higher than that of the residual biomass. Compared to the starting *Sargassum* biomass, the production of biomethane was significantly promoted with the high temperature aqueous treatment, increasing the biomethane yield from 23 m^3/ton DW to 102 m^3/ton DW, when corrected on the recovered dry matter in the slurry after treatment. The biomethane potential of the untreated *Sargassum* biomass observed in this study was relatively lower than reported previously for *Sargassum* spp. biomass (40–208 m^3/ton VS) [17,18,69,70]. Prior studies looking into high temperature aqueous treatment have reported improved biomethane production consistent with the results in this study, albeit to varying degrees, with reported yields that range from 60 to 170 m^3/ton VS, depending on anaerobic digestion conditions and, indirectly, the biochemical composition of the starting *Sargassum* [17,18]. The data reported in literature shows that suitability of raw *Sargassum* biomass for biomethane production, without additional treatment, may depend on the biochemical composition of the biomass source as well as the digestion technology used or approach followed. Promotion of the digestibility through aqueous treatment at high temperature was evidently promoted by the depolymerisation/solubilisation of the biomass, since the fractions in this study that included solubilised dry matter (treated slurry and hydrolysate) reported both the highest COD and biomethane potential values. The productivity of biomethane from the residual biomass was higher than that from the starting biomass, but still low for what could be considered a good quality AD feedstock.

Prior work has shown that aqueous treatment with the objective to

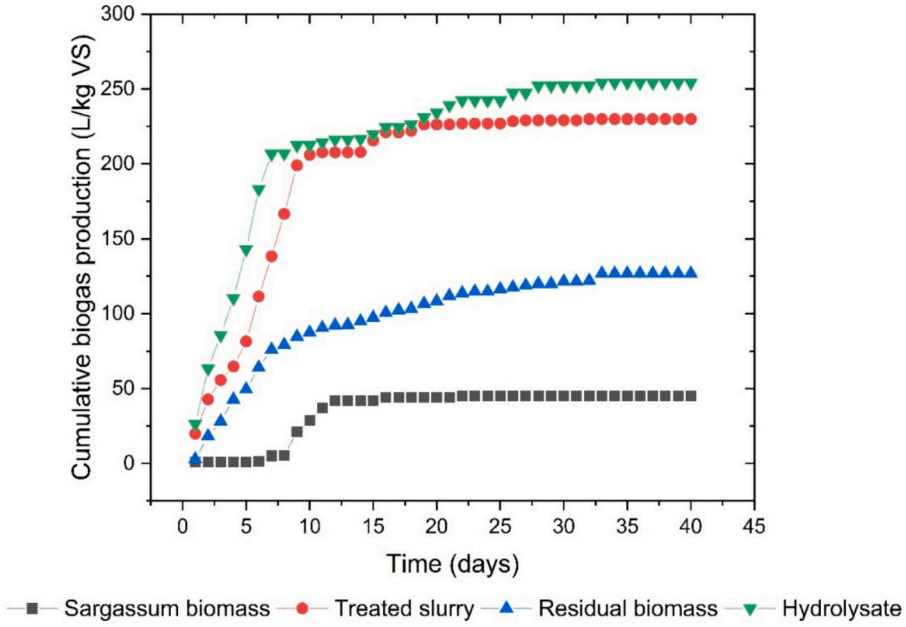

Fig. 4. Cumulative biogas production per kg of volatile solids (VS) from *Sargassum* biomass and treated fractions over 40 days.

Table 8
Biomethane potential characteristics of *Sargassum* biomass and treated fractions.

		Sargassum biomass	Treated slurry	Hydrolysate	Residual biomass
Volatile solids content (% DW)		75.4 ± 0.7	66.5 ± 0.3	60.0 ± 0.1	90.5 ± 0.5
Chemical oxygen demand (mg/g DW)		149.6 ± 3.5	1259.0 ± 217.4	621.5 ± 2.3	91.0 ± 7.2
Biomethane potential (28 days)	(m^3/ton VS)	31.1 ± 3.8	153.3 ± 10.0	170.2 ± 4.5	79.7 ± 6.7
	(m^3/ton DW)	23.5 ± 2.9	102.0 ± 6.7	102.1 ± 2.7	72.2 ± 6.1
	(m^3/ton DW equivalent *Sargassum* biomass)		84.4 ± 5.5	51.8 ± 1.4	27.8 ± 2.3

improve anaerobic digestibility of *Sargassum* biomass requires optimisation, since too high severity (i.e. combination of high temperature and/or long treatment time) can lead to degradation reactions of solubilised compounds (e.g. Maillard reactions, humin formation) and the formation of inhibitory compounds [17]. Furthermore, the present work shows that the higher digestibility is mostly found in the solubilised matter present in the hydrolysate fraction. This means that biorefinery concepts in which valorisation of *Sargassum* biomass through fucoidan recovery from hydrolysates combined with biomethane production from residual biomass could still require other means of boosting AD efficiency and biogas productivity, such as co-digestion with other biogenic feedstocks [70].

Digestate composition and quality is another important aspect of the utilisation of *Sargassum* biomass and/or treated fraction thereof for AD. Seaweeds in general are well known for accumulating heavy metals from seawater and high levels of e.g. arsenic have been observed in *Sargassum* spp. biomass [3]. Digestates are often applied in soil and thus heavy metal levels in AD feedstocks can hinder their utilisation. The *Sargassum* biomass used herein had a high macro-nutrient content (K > Na > Ca > Mg >> P), which accounted for approx. 14 % DW of the biomass (SI Table 8). Most of these macro-nutrients were released from the biomass into the hydrolysate during the high temperature aqueous treatment (SI Fig. 3). Other metals found in large quantities in the biomass were Sr > Si > B > Al > Fe > As > Mn > Ba > Ti > Zn, in concentrations between 1847 and 10 mg/kg DW (SI Table 7). These metals remained mostly in the residual biomass after the aqueous treatment, thus some of them were found in higher concentrations in the residual biomass than in the starting biomass. In the context of European regulations, final levels of Cd, hexavalent Cr and inorganic As can limit the suitability of the derived digestates as fertilisers and must be closely monitored in both feedstock and derived digestates [71] (SI Table 8).

3.5. Feasibility and technoeconomic perspective of valorisation routes

The experimental findings from this study were utilised as basis for a simplified technoeconomic analysis to compare the potential routes for valorisation of *Sargassum* biomass in the Caribbean. Three concepts were compared to a benchmark scenario in which *Sargassum* is used as feedstock for biogas production directly without further treatment (Fig. 1). Concept 1 considered that alginate and fucoidan are co-produced via mildly acidic, low temperature aqueous treatment and alkaline extraction, respectively, and where solid residues are used for biogas

Table 9
Summary of capital investment (TCI), return on investment (ROI), and annual revenues for *Sargassum* biomass valorisation concepts.

Concept	Products	First process step	TCI (M€)	ROI (%)	Revenues (M€/year)
Concept 1	Alginate + fucoidan + biogas + digestate	Low temperature aqueous treatment	33.2	28	9.18
Concept 2	Fucoidan + biogas + digestate	High temperature aqueous treatment	12.8	26	3.33
Concept 3	Biogas + digestate	High temperature aqueous treatment	3.8	12	0.45
Benchmark	Biogas + digestate	None	2.3	16	0.36

production. Concept 2 involves the production of fucoidan through high temperature aqueous treatment and biogas production from solid residues. In contrast, concept 3 considers biogas production via high temperature aqueous treatment. The findings of the technoeconomic analysis are summarised in Table 9. The benchmark scenario, a biogas-only route without any treatment of the biomass, yields an annual output of 98 t of biogas and requires a capital investment of €2.3 million leading to a Return on Investment (ROI) of 16 %. In this scenario, biogas accounts for 57 % of the annual revenue, with a considerable portion of that derived from the sale of digestate (€0.20 per kg).

As shown in Section 3.4, the implementation of high temperature aqueous treatment promotes the digestibility of the biomass and thus leads to higher biomethane production (437 t biogas per year) and higher revenues (0.45 M€/year). However, this scenario requires a higher total capital investment (TCI), resulting in slightly lower ROI (12 %). The co-production of high value polysaccharides along with biogas improves profitability but to a moderate extent. Concept 1, which focuses on the co-production of alginate and fucoidan, had the highest profitability with a ROI of 28 % and the highest revenues (9.18 M€/year), in despite of the considerably higher TCI required. Concept 2, which only considers the production of fucoidan in addition to biogas/digestates, had almost the same ROI (26 %) albeit the lower order of revenues (3.33 M€/year). The similar profitability of concepts 2 and 3 was caused by trade-offs in terms of capital investment required for less processing steps required in concept 3 and slightly higher production of biogas and digestates. This is despite the lower fucoidan yield assumed in concept 3 (112 t fucoidan per year) compared to concept 2 (172 t fucoidan and 580 t alginate per year).

Naturally the profitability of these concepts was largely driven by the assumed market values of the products. Alginate selling price can vary significantly from a "low end" market of hydrocolloids (0.4–1.3 €/kg) [72] to a "high end" market of pharmaceutical applications (12–49 €/kg) [73]. The same applies to fucoidan, where applications can range from nutraceuticals (7 to 22 €/kg) [74] to pharmaceuticals (50 to 147 €/kg) [75]. Negative aspects of purity, molecular weight, colour and rheological and bioactive properties can hinder the introduction of *Sargassum*-derived polysaccharides to any of these markets. While the prices assumed in this study are deemed moderate (8 and 30 €/kg), the study assumes that the products comply with quality standards expected for such markets. However, arriving to the required properties may need additional purification/separation unit operations currently not included in the technoeconomic assessment, that in principle, would reduce the overall product yield and add significant capital and operational expenses.

A sensitivity analysis was performed to illustrate the impact of product yields/prices and increased requirement in capital investment (SI Fig. 8). The ROI can decrease down to 18 % if TCI increases by 50 % given additional operational units required for purification. Similarly, a 50 % decrease on either fucoidan or alginate yields or their selling prices can lead to a similar impact in profitability. A simultaneous increase in both TCI by 50 % and decrease of product yields by 50 % would lead to a concept with much lower profitability (ROI = 7.6 %). In the estimations presented in this study, fucoidan and alginate contribute almost to the same extent to revenues (52 % and 47 %, respectively), thus having almost the same impact on the ROI upon variations of product yield (SI Fig. 4). However, this is a feature of the relative product yields observed experimentally and the selected selling prices in this study.

Variations in the valuation of digestate had a limited impact on concepts 1 and 2 given that the bulk of the profits in these scenarios would depend on the polysaccharides. However, in a situation where digestate cannot be used as fertiliser due to strict regulations or contamination issues, concepts 3 and the benchmark scenario would become unprofitable, reflecting negative ROIs (−9 and − 22 %, respectively).

These results show the potential to achieve better economic performance through the cascading approach but it does illustrate the risks and sensitivities associated to product quality and selling prices in the case of polysaccharides derived from *Sargassum* biomass. In the interpretation of the findings of this economic outlook, it is also important to consider some other key limitations. Equipment size, energy consumption, and installation specifications are based on vendor data and engineering assumptions and should be considered as preliminary. Moreover, considerable uncertainties exist regarding market forecasts for fucoidan, alginate and derived digestates used as fertiliser, as prices fluctuate significantly across regions and are heavily influenced by the quality of the respective products.

Production of alginate or fucoidan from wild Caribbean *Sargassum* is not yet at large commercial scale. While some biorefining concepts for the utilisation of *Sargassum* biomass are being developed at different technology readiness levels (e.g. Origin by Ocean [76], MacroCarbon [77], alginate production from *Sargassum* spp. in India [78]), significant challenges for the commercialisation of valorisation routes for *Sargassum* remain. Factors such as lower polysaccharide product yields, lower molecular weight in polysaccharide products, higher polyphenol content in extracts, and generally poorer product quality when compared to established feedstocks for commercial alginate such as *Laminaria* sp. and *Macrocystis pyrifera* make it challenging for *Sargassum* to compete in existing alginate markets.

Additionally, there are significant operational risks that are not fully addressed in the present simplified techno-economic assessment. These risks include irregular and unpredictable beach landings, the spatial dispersion of the biomass, rapid degradation and microbial spoilage after landing, as well as the high moisture content of the biomass. Together, these factors create substantial requirements for front-end logistics and pre-processing, including harvesting, stabilisation, and grinding prior to processing. This can increase OPEX and transportation burdens, which could further diminish the ROI of the concepts. Whenever feasible, sun drying can be used as a low-cost stabilisation method. However, this method is dependent on weather conditions, is time-consuming, and may result in feedstock contamination or spoilage, which can negatively impact storage, transport, and product quality. While solar dryers can reduce drying times and improve product uniformity at a modest capital cost, they still require sufficient space and labour. While new industrial concepts, such as decentralized or offshore cultivation and stabilisation approaches, are being explored by companies for large-scale carbon removal using cultivated macroalgae, these approaches have not yet been proven at an industrial scale for pelagic Caribbean *Sargassum*. Therefore, the associated risks of biomass logistics and product quality should be explicitly considered as key uncertainties when evaluating the economic feasibility of the valorisation routes discussed here.

4. Conclusions

The present study investigates valorisation routes of *Sargassum* spp. biomass that include polysaccharide extraction and biomethane production enabled through low and high temperature aqueous treatments. Based on the saccharide content, the *Sargassum* biomass used in the present study was found to have low levels of alginate, fucoidan and cellulose compared to main commercially alginate-producing brown seaweed species. Low yields of alginate and fucoidan (145 and 43 g/kg DW biomass) were obtained from the biomass via sequential extraction enabled by low temperature acidic aqueous treatment. These fractions had relatively low molecular weights and high polyphenol content as evidenced by the brown colour of the extracts.

High temperature aqueous treatment improved the extraction efficiency of fucoidan based on the fucose content found in hydrolysates; however, the molecular weight of the saccharide was decreased (< 10 kDa), thus crude fucoidan yields were not improved by the higher severity of the treatment. Furthermore, alginate extraction yield and composition was negatively affected by the higher temperature treatment. Anaerobic digestion tests of untreated and treated fractions of

Sargassum biomass showed that high temperature aqueous treatment can increase the biomethane production by up to 3.5 times. This increase was due the release or solubilisation of organic compounds and the increase in the COD content of the biomass. This indicated that the hydrolysate fraction, containing fucoidan, was the energy-rich fraction most suitable for AD.

A simplified technoeconomic analysis points to promising valorisation pathways for *Sargassum* biomass in the Caribbean. Under a scenario of processing 4000 t of dried biomass annually, the analysis suggests that concepts incorporating polysaccharide extraction may increase profitability, with ROIs of 26 % (only fucoidan) and 28 % (fucoidan and alginate), compared to scenarios where only biogas and digestates are produced (ROIs 12 % and 16 % with and without high temperature aqueous treatment). High temperature treatment did not lead to a higher ROI compared to direct utilisation of *Sargassum* biomass in AD. Nevertheless, implementation of this additional step may generate higher revenues and biogas production. Further, the analysis also highlights the sensitivity of these valorisation pathways to fluctuations in product prices and yields, particularly in relation to the risks posed by inconsistent or poor product quality, including purity, molecular weight, colour, and rheological and bioactive properties. On the other hand, scenarios that centre on biogas production rely heavily on the suitability of digestates for use as fertiliser for their profitability.

CRediT authorship contribution statement

Karla Dussan: Writing – review & editing, Writing – original draft, Visualization, Supervision, Methodology, Formal analysis, Conceptualization. **Paulina S. Birgersson:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis. **Stefania Luzzi:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis. **Olav A. Aarstad:** Writing – review & editing, Investigation, Formal analysis. **Esther Cobussen-Pool:** Supervision, Methodology, Investigation. **Tim Koster:** Investigation. **Heather E. Wray:** Writing – review & editing, Project administration, Conceptualization. **Finn L. Aachmann:** Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition, Formal analysis.

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Declaration of competing interest

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Appendix A. Supplementary data

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Data availability

Data will be made available on request.

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