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Valorisation of macroalgae via the integration of hydrothermal carbonisation and anaerobic digestion

Aaron E. Brown[a], Gillian L. Finnerty[a], Miller Alonso Camargo-Valero[b,c], Andrew B. Ross[a,*]

[a] School of Chemical and Process Engineering, University of Leeds, Leeds LS2 9JT, UK
[b] BioResource Systems Research Group, School of Civil Engineering, University of Leeds, Leeds LS2 9JT, UK
[c] Departamento de Ingeniería Química, Universidad Nacional de Colombia, Campus La Nubia, Manizales, Colombia

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ABSTRACT

This study investigates the integration of hydrothermal carbonisation (HTC) with anaerobic digestion (AD) as a valorisation route for two macroalgae species; *S. latissima* (SL) and *F. serratus* (FS). HTC reactions were conducted at temperatures of 150 °C, 200 °C and 250 °C, with resulting hydrochars, process waters and hydrothermal slurries assessed for biomethane potential yields. Un-treated SL generated similar biomethane levels compared to all SL slurries. Whereas all FS slurries improved biomethane yields compared to un-treated FS. Hydrochars represent a greater energy carrier if used as a solid fuel, rather than a feedstock for anaerobic digestion. Integrating HTC and AD, through hydrochar combustion and process water digestion has a greater energetic output than anaerobic digestion of the un-treated macroalgae. Treatment at 150 °C, with separate utilisation of products, can improve the energetic output of *S. latissima* and *F. serratus* by 47% and 172% respectively, compared to digestion of the un-treated macroalgae.

1. Introduction

In the shift towards a bio-based economy there is an ever-increasing demand for the generation of renewable biofuels from feedstocks which do not compete for land with terrestrial food and feed crops (Kraan, 2013). The use of macroalgae to produce third generation biofuels could overcome inherent disadvantages of utilising first and second generation crops (Montingelli et al., 2015). Macroalgae biomass production yields are 2–20 times greater than terrestrial biomass (Bruhn et al., 2011) due to increased growth rates linked to higher photosynthetic efficiency (Kraan, 2013). Additionally, the use of macroalgae can lead to a reduced demand for fresh water, arable land and fertiliser (Torres et al., 2019). Despite the advantages of using macroalgae over terrestrial biomass, inherent physiochemical properties hinder the use of seaweeds in conventional thermal conversion technologies. Such properties include a high moisture content and a high inorganic content, resulting in a lower heating value than terrestrial crops and problems with corrosion and fouling (Ross et al., 2008). The presence of high concentrations of alkali metals within macroalgae creates a high tendency for slagging, fouling and corrosion during utilization during combustion, pyrolysis or gasification (Smith and Ross, 2016).

Hydrothermal carbonisation (HTC) involves the conversion of biomass in hot compressed liquid water, typically between 180 °C and 250 °C at elevated autogeneous pressure (Nizamuddin et al., 2017). Under these conditions, water remains in a subcritical state (Kruse et al., 2013) to facilitate a cascade of simutaneous reactions (Funke and Ziegler, 2010). Biomass is converted to an energy densified solid; hydrochar, an aqueous phase; process water and a small proportion of gaseous phase. Traditionally, the majority of research has focused on the generation of hydrochar from HTC; a carbon-rich solid with high porosity and functionality. Such properties allows for the application of hydrochars for a variety of purposes (Fang et al., 2018), including; soil amendment, absorbant, energy storage and as a solid-combustion fuel. HTC has the capacity to process feedstocks with a high moisture content; posing a significant advantage for the treatment of macroalgae. Hydrochar produced from macroalgae has a similar heating value to that of a low ranking coal, as well as significant demineralisation, compared to the original macroalgae (Smith and Ross, 2016, Kantarli et al., 2019), suggesting its safe use as a solid combustion fuel. The process water generated from HTC is a complex mixture of solubilised organics and inorganics from the original biomass (Wirth and Mumme, 2013; Erdogan et al., 2015). The carbon content of the process water often represents a significant proportion of the carbon originally in the biomass (Becker et al., 2014). To further enhance the energetic yield, HTC process waters can be anaerobically digested to generate biomethane. Previous studies have investigated the digestion of HTC

* Corresponding author.
E-mail address: a.b.ross@leeds.ac.uk (A.B. Ross).

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process waters from digestates (Aragón-Briceño et al., 2017, Parmar and Ross, 2019;), corn silage (Wirth and Mumme, 2013) orange pomace (Erdogan et al., 2015) and microalgae (Marin-Batista et al., 2019).

Anaerobic digestion is a promising, well established technology; generating biogas from the degradation of organic matter under oxygen-free conditions (Ward et al., 2008) through a casade of bacterial and *Archaeal* metabolic pathways (Bharathiraja et al., 2016). Biogas can be used directly to generate heat or electricity, or upgraded to biomethane to be injected directly into the national grid, or used as a transport fuel. A number of studies have investigated the biomethane generation from macroalgae (Adams et al., 2011; Montingelli et al., 2015; Allen et al., 2015; Tabassum et al., 2017). However, of the ten seaweed species tested by Allen et al. (2015) only four species had an anaerobic biodegradability $>$ 50%.

Integration of hydrothermal processing with anaerobic digestion is gaining interest to maximise the energetic output from different feedstocks. However, despite numerous reports in the literature, it is still uncertain which integration strategy is the most effective approach for maximising energy recovery. Separation of hydrochars and process waters after hydrothermal treatment for different applications is one method to integrate HTC and AD. Few studies have investigated the biomethane generation from hydrochars due to their high recalcitrance to microbial digestion (Mumme et al., 2014). Despite this, Luz et al. (2018) found significant yields of biomethane from spent coffee ground hydrochar, however, the biomethane yields were not compared to untreated coffee grounds. This approach would require an alternative application for the process water, such as re-circulation into HTC (Catalkopru et al., 2017) or as a nutrient-rich fertiliser (Chen et al., 2017).

A more common approach is to separate the hydrochar for use as a solid combustion fuel and subsequent anaerobic digestion of the process waters (Smith and Ross, 2016; Aragón-Briceño et al., 2017; Paul and Dutta, 2018; Marin-Batista et al., 2019). However, there is only limited data on the properties of seaweed derived process waters and the most extensive studies are based on predictive yields (Smith and Ross, 2016). Wang et al. (2019) investigated the influence of process water recirculation on the HTC of a *Laminaria* species, including biomethane generation from process water digestion. However, this was only conducted at a single HTC temperature; 220 °C. Anaerobic digestion of process waters bypasses the hydrolysis stage, which is often regarded as the rate limiting step (Monlau et al., 2013), therefore faster degradation rates can be assumed. However, severe pre-treatments cause the formation of inhibitory by-products, including; furfural, furfuryl alcohol, 5-HMF, formic acid, acetic acid and propionic acid (Nakason et al., 2017). The formation of these compounds reduce biomethane yields (Erdogan et al., 2015; Marin-Batista et al., 2019). Despite this, Heidari et al. (2020) recently simulated the energetic output of combustion compared to HTC-AD; suggesting HTC-AD is a more suitable conversion option for feedstocks with high moisture and initial low HHV values.

Another approach is to hydrothermally pre-treat feedstocks at lower HTC temperatures; between 100 °C −200 °C (Ding et al., 2017; Lin et al., 2019; Ding et al., 2020) and generate biomethane from the slurry (mixed hydrochar and process water). Ding et al. (2020) found low temperature (140 °C) hydrothermal treatment to be the optimal pre-treatment for two-stage digestion of the macroalgae *Laminaria digitata* when compared with a range of pre-treatments, such as; dilute acid pre-treatment and enzymatic hydrolysis. An optimal pre-treatment temperature of 140 °C was found for both food waste (Ding et al., 2017) and seaweed species *S. latissima* (Lin et al., 2019), to produce enhanced biomethane yields from a two-stage process, linked to optimal carbohydrate solubilisation. Increasing the temperatures above 140 °C reduced biomethane yields due to inhibitory Malliard reactions with food waste and inhibitory by-product formation from *S. latissima*. Wang et al. (2018) found hydrothermally treating rice straw at 210 °C significantly reduced biogas yields by 30%, probably due to the inhibitory nature of the hydrochar. Typically hydrothermal slurries generated at higher temperatures are not recommended for anaerobic digestion.

Zhao et al. (2018) investigated the integration strategies of HTC and AD; digesting food waste hydrochar, process water and a mixed slurry. The addition of hydrochar to the process water improved biomethane yields by 153% compared to digestion of the process water alone, due to the hydrochar acting as a surface for microbial interaction. However, these results were not compared to biomethane yields from the untreated food waste.

The aim of this study is to perform an experimental assessment of the different integration strategies for linking hydrothermal conversion with anaerobic digestion for two types of brown macroalgae. These include a subtidal kelp (*Saccharina latissima*) and an intertidal wrack (*Fucus serratus*), common to the UK. The different integration strategies investigated include; (i) anaerobic digestion of the raw macroalgae, (ii) anaerobic digestion of mixed slurries of hydrochar and process water, (iii) anaerobic digestion of hydrochar alone to understand its' digestion behaviour and (iv) anaerobic digestion of process waters alone and subsequent combustion of the hydrochars. This research compares for the first time, the energetics of each of these integration strategies on the same feedstocks, it investigates this over a wider range of temperatures than previously reported and it includes an assessment of a previously under reported feedstock (*Fucus serratus*), extending knowledge on the hydrothermal processing of wracks. This research therefore aims to understand the influence of process variables on the conversion of macroalgae and identify the optimum valorisation approach for production of bioenergy from macroalgae.

2. Materials and methods

2.1. Sample collection and storage

Fucus serratus was collected from Aberystwyth, Wales, UK in June 2015. *Saccharina latissima* was collected from Beadnell Bay, Northumberland, UK in June 2017. Samples were freeze dried and stored under nitrogen gas for preservation. Dried samples were homogenised and the particle size reduced to $<$ 1 mm. Solid samples were homogenised to a particle size of $<$ 100 μm using a RETSCH Cryomill for subsequent proximate and ultimate analysis. Inoculum samples were collected from an AD facility at Esholt wastewater treatment plant (Bradford, UK). The inoculum was passed through a 1 mm screen to remove large particulate matter and stored at 4 °C until needed.

2.2. Hydrothermal carbonisation reactions

Hydrothermal carbonisation (HTC) reactions were conducted in a 600 mL non-stirred Parr reactor inside a custom-made quartz glass liner. Reactions were carried out in triplicate using 20 g of dried seaweed mixed with 200 mL distilled water. Dried biomass was used in HTC reactions to prolong storage of biomass and facilitate accurate controlling of conditions. Reactions were conducted at 150 °C, 200 °C and 250 °C with a retention time of 60 min once the desired temperature was reached. The temperature was ramped at approximately 8 °C per minute using an external heater with PID controller. Reactors were left to air-cool to around 25 °C, after which the reactor was vented to release the gaseous products and the reactor was opened. The products (hydrochar and process water) were recovered by Büchner filtration through a Whatman Grade 4 filter paper. Collected hydrochars were subsequently dried at 60 °C for 24 h, with moisture losses measured gravimetrically and recorded losses attributed to the process water. Hydrochar yields were determined according to Equation 1. Process

water masses were determined according to Equation 2; a summation of the mass of process water collected from Büchner filtration (Pw^A) and mass of process water lost from the drying of hydrochars (Pw^B). Products of reactions with the same conditions were blended to ensure enough material for the biomethane potential experiments.

$$Hydrochar\ Yield\ (\%) = \frac{Mass\ of\ Dried\ Hydrochar\ (g)}{Mass\ of\ Dried\ Seaweed\ (g)} \times 100 \quad [1]$$

$$Process\ Water\ Mass\ (g) = Pw^A + Pw^B \quad [2]$$

2.3. Biomethane potential

The experimental biomethane potential (BMP_{ex}) of the un-treated seaweeds and hydrothermal products was conducted using an AMPTS II (Bioprocess Control). The hydrothermal products include; hydrochars, process waters and mixed slurries of both hydrochars and process waters. Samples and inoculum were loaded into the reactors in a 2:1 inoculum-to-substrate ratio on a COD basis for aqueous samples (process waters) and a VS basis for raw seaweeds, hydrochars and slurries. The contents of reactors were not pH adjusted. Inoculum was incubated in a 37 °C water bath for 48 h prior to setting up the BMP tests to reduce residual methane emissions. All reactors were flushed with nitrogen gas to ensure anaerobic conditions. Reactors were maintained at 37 °C for 30 days and automatically agitated for 60 s every 10 min. Blank reactors containing only inoculum were run in parallel to account for residual methane emissions. The volumes of methane generated were normalised to the concentration of COD or VS added using Equations 3 and 4 respectively. Samples and blanks were tested in duplicate, with the mean values displayed.

$$BMP_{ex} = \frac{Volume\ CH_4\ from\ Sample\ (mL) - Volume\ CH_4\ from\ Blank\ (mL)}{COD\ Concentration\ \left(\frac{g}{L}\right) \times Volume\ of\ Sample\ (L)} \quad [3]$$

$$BMP_{ex} = \frac{Volume\ CH_4\ from\ Sample\ (mL) - Volume\ CH_4\ from\ Blank\ (mL)}{VS\ Concentration\ \left(\frac{g}{L}\right) \times Volume\ of\ Sample\ (L)} \quad [4]$$

The biodegradability index (BI) is an indication of methane conversion efficiency of a sample (Wall et al., 2013). BI of solid samples was determined according to Equation 5, using the Boyle's equation to calculate theoretical biomethane potential (BMP_{th}) (Smith and Ross, 2016).

$$BI\ (\%) = \frac{Experimental\ Biomethane\ Potential\ (BMP_{ex})}{Theoretical\ Biomethane\ Potential\ (BMP_{th})} \times 100 \quad [5]$$

2.4. Analytical methods

Proximate analysis of the samples was determined using a thermogravimetric analyser (TGA/DSC 1, Mettler Toledo). The heating profile of the TGA was ramped from 25 °C to 105 °C, retained for 10 min and then subsequently ramped to 900 °C, held for 10 min under nitrogen gas and a further 10 min under air. Ultimate analysis was determined using an elemental analyser (Flash 2000, Thermo Scientific) measuring CHNS and oxygen directly. Both hydrogen and oxygen were corrected to account for moisture content. The higher heating value (HHV) of solid samples were calculated according to Dulong's equation (Smith and Ross; 2016) as shown in Equation 6. The removal of inorganic material from the hydrochars following hydrothermal conversion was determined using X-ray fluorescence spectrophotometry (XRF, ARL PERFORM'X, Thermo Scientific).

$$HHV = (0.3383 \times \%Carbon) + (1.422 \times \%Hydrogen) - \left(\frac{\%Oxygen}{8}\right) \quad [6]$$

Due to the complex ashing behaviour of macroalgae, the volatile solid (VS) content of un-treated seaweeds and hydrochars was determined through the summation of volatile matter and fixed carbon contents (on an as received basis) from the TGA proximate analysis. The residual ash produced at 550 °C contains between 1.5 and 3.0 % carbon (Anastasakis, 2011), which can lead to an underestimation of VS content, subsequently influencing interpretation of biomethane potential yields. Using a TGA ashing temperature of 900 °C allows for complete removal of residual carbon in the ash. Volatile solid (VS) was determined for process waters according to APHA, American Public Health Association. (2005). The VS of hydrochars and process waters was determined separately, then re-introduced as a slurry based on the masses recorded in Equations 1 and 2.

Chemical oxygen demand (COD) was determined using HACH Lange cuvettes LCK014. Total organic carbon (TOC) was measured by difference using a HACH IL 500 TOC-TN analyser. The amount of carbon solubilised in the process water was calculated through the percentage difference of the total mass of carbon in the original biomass and the total mass of carbon in the residual process water. Total phenols (TP) was determined using HACH Lange cuvettes LCK346. The pH of samples was measured using a HACH pH meter.

Volatile fatty acid (VFA) concentration was measured using gas chromatography with flame ionisation detection (GC-FID) using a DB-FFAP column, Length-30 m, Dia-0.32 mm, Film Thickness-0.5 μm. Helium was used as the carrier gas at a flow rate of 10 mL/min. An autosampler injected 10 μl of sample using a 5:1 split ratio with the inlet maintained at 150 °C. The oven heating profile was hold at 60 °C for 4 mins, ramp at 10 °C/min to 140 °C, ramp at 40 °C/min to 200 °C and hold for 5mins. The FID detector was maintained at 200 °C with Nitrogen make-up gas. Aqueous samples were prepared for GC-FID by acidifying to pH 2.0 ± 0.1 with phosphoric acid, centrifuging at 14,000 rpm (16,000xg) for 5 mins and finally passing the supernatant though a 0.2 μm syringe filter.

2.5. Energy balance

The energy input required to heat the HTC reactor was calculated according to Lin et al., (2019); modified to a starting material of 1 kg of dried seaweed, using a 10% HTC solid loading ratio. A specific heat capacity of 1,500 J/kg/K is assumed for both seaweed species; the median value used by Green *et al.* (2020) for a range of biomass. The energy output of hydrothermally treated samples was calculated based on 1 kg of dried seaweed for un-treated macroalgae and macroalgae treated at 150 °C, 200 °C and 250 °C. The energy output for biomethane production from un-treated macroalgae was based upon Equation 7. The energy output for biomethane generation from the process waters was based upon Equation 8, based on the assumptions that 1 mL water equals 1 g and HHV of methane being 39.8 MJ/m^3. The energy output for combustion of the hydrochars was based upon Equation 9. The HHV of the hydrochars is on an as received basis. The net energy balance was determined by Equation 10; assuming an 85% heat recovery efficiency for the HTC stage (Yuan et al., 2019). The energy output is the combined energy from combustion of the hydrochars plus the energy from the biomethane generated from the process water. An energy return on energy investment (EROI) calculation was conducted using Equation 11, again assuming an 85% heat recovery efficiency from the HTC stage.

$$Macroalgae\ Energy\ \left(\frac{MJ}{kg}\right) = \frac{VS\ (kg) \times BMP_{ex}\ \left(\frac{LCH_4}{kgVS}\right)}{1000} \times 39.8 \quad [7]$$

$$Process\ Water\ Energy\left(\frac{MJ}{kg}\right) = \frac{Mass\ of\ Process\ Water\ (kg) \times COD\left(\frac{g}{L}\right) \times BMP_{ex}\left(\frac{mLCH_4}{gCOD}\right)}{1,\ 000,\ 000} \times 39.8 \quad [8]$$

$$Hydrochar\ Energy\left(\frac{MJ}{kg}\right) = Hydrochar\ Yield\ (kg) \times HHV\left(\frac{MJ}{kg}\right) \quad [9]$$

$$Net\ Energy\ Balance\left(\frac{MJ}{kg}\right) = Energy\ Output\left(\frac{MJ}{kg}\right) - \left(Energy\ Input\left(\frac{MJ}{kg}\right) \times 0.15\right) \quad [10]$$

$$EROI = \frac{Energy\ Output\left(\frac{MJ}{kg}\right)}{\left(Energy\ Input\left(\frac{MJ}{kg}\right) \times 0.15\right)} \quad [11]$$

2.6. Error and statistical analysis

All HTC experiments were conducted in triplicate. BMP_{ex} runs and analyses were conducted in duplicate, unless otherwise specified. TOC analysis involved triplicate injections. Average values are reported and standard deviation presented as error bars on figures. Analysis of variance (ANOVA) was carried out on the final BMP_{ex} value, grouping each hydrothermal product separately; hydrochar, process water and slurry. ANOVA was calculated using the SPSS Statistics software (version 23) with additional Tukey *post hoc* test to identify significant differences to a confidence level of $p < 0.05$.

3. Results and discussion

3.1. Characteristics of hydrothermal products

3.1.1. Hydrochars

Raw seaweed and hydrochar characteristics are displayed in Table 1. Energy densification of the solid residue (hydrochar) can be seen with increasing HTC processing temperature across both seaweed species; with increasing fixed carbon, carbon and HHV values. The energy densification is a result of de-oxygenation of the solid (Smith and Ross, 2016, Kantarli et al., 2019) which can be seen through the reducing O:C. HHV of hydrochars produced at 250 °C increased by 65% and 57% for *S. latissima* (SL) and *F. serratus* (FS) respectively, compared to the original biomass, with FS250-char showing the highest calorific value of 22.3 MJ/kg. Kantarli et al. (2019) report a HHV for *F. serratus* hydrochar ranging from 23.2 to 26.6 MJ/kg at a temperature range of 200–250 °C; the highest HHV across three seaweed species. Energy densification (ED) increases with increasing HTC temperature, with SL250-char showing the greatest ED of 1.65. Hydrochars in this study show an increasing ash content with increasing HTC temperature, as the ash becomes concentrated. Hydrochar yields are dependent on both feedstock type and HTC temperature (Smith et al., 2016), with decreasing yields with increasing HTC temperature. Hydrochar yields (18–39%) found by Smith and Ross (2016) for a variety of macroalgae species are similar to those found in this study. Macroalgae char yields are significantly lower than alternative feedstocks, such as lignocellulose 40–70% (Smith et al., 2016), corn stover 36–63% (Machado et al., 2018), orange pomace 37–54% (Erdogan et al., 2015) and cassava rhizome 51–57% (Nakason et al., 2018). A similar finding is reported by Kantarli et al. (2019). Low hydrochar yields suggests a high solubilisation of organic and inorganic into the process waters which is reflected by over 50% of the original carbon in the seaweeds being solubilised in the process waters for most samples, shown in Table 2. Consequentially, in order to justify hydrothermal processing of seaweed the energetic value of the process waters must be recovered to ensure an energetically feasible process.

3.1.2. Process waters

The composition of the process waters is displayed in Table 2. The total organic carbon of macroalgae process waters (13.36–16.84 g/L) is consistently high compared to other feedstocks; wheat straw and woody biomasses (4–9 g/L) (Becker et al., 2014) and microalgae (11.5–13.1 g/L) (Marin-Batista et al., 2019). High TOC content of the seaweed process waters suggests a readily degradable structure of macroalgae under HTC conditions, which solubilise into the process water. There appears to be no real trend between HTC temperature and TOC content. Erdogan et al. (2015) finds a linear decrease in TOC with increasing HTC temperature, due to direction towards the gaseous phase formation. Alternatively, Becker et al. (2014) suggest TOC concentration is largely unaffected by HTC process severity; however, this does affect the composition of the process water. Table 2 shows a significant amount of carbon is solubilised within the process waters; above 50% for all *S. latissima* process waters. This re-iterates the significance of extracting value from the process water, rather than focussing exclusively on the hydrochar.

The solubilised intermediates of the HTC process; sugars and volatile fatty acids are metabolised by anaerobic microorganisms to generate biomethane. Table 2 shows an increase in the volatile fatty acid content of the process waters between 150 °C and 200 °C. Higher

Table 1
Composition of solid samples; un-treated seaweeds and hydrochars.

Feedstock	HTC Temperature (°C)	Proximate Analysis (%) *db*			Ultimate Analysis (%) *db*					O:C[1]	C:N[1] (*db*)	VS(%)	HHV (MJ/kg) (*db*)	ED	BMP_{th}
		Hydrochar Yield (%)	Volatile Matter	Fixed Carbon	Ash	C	N	H	S	O	(*daf*)		(*ar*)			(mL CH_4/g VS)
Saccharina latissima	0	–	75.8	13.3	10.9	33.0	1.9	2.9	ND	23.6	0.72	17.4	82.3	12.4	–	482
	150	37.5	73.1	16.1	10.8	41.1	2.8	4.4	ND	26.1	0.63	14.7	85.3	16.9	1.36	537
	200	28.4	69.0	17.3	13.8	43.2	2.2	3.7	ND	20.3	0.47	19.6	84.2	17.4	1.40	611
	250	22.0	62.5	18.7	18.8	48.3	2.2	4.2	ND	15.2	0.32	22.0	79.6	20.4	1.65	717
Fucus serratus	0	–	70.8	11.8	17.4	35.6	2.0	4.0	ND	27.9	0.78	17.8	77.7	14.2	–	479
	150	44.7	71.4	16.9	11.7	46.8	3.0	3.8	ND	25.0	0.53	15.6	84.5	18.1	1.27	558
	200	32.7	66.7	19.2	14.1	51.0	2.8	4.3	ND	20.4	0.40	18.2	83.7	20.8	1.46	649
	250	27.6	61.8	19.2	19.1	54.6	2.4	4.1	ND	15.0	0.28	22.8	79.5	22.3	1.57	730

db = dry basis. *daf* = dry ash free. *ar* = as received. HHV = higher heating value. BMP_{th} = theoretical biomethane potential. ND = not detected. [1]calculated on a mass basis. ED = energy density (Zhao et al., 2018), calculated as $\frac{HHVHydrochar}{HHVSeaweed}$

Table 2
Process water composition from HTC reactions.

Feedstock	HTC Temperature (°C)	COD	TOC	Total Phenols	Total Volatile Fatty Acids (mg/L)				pH	C% from original Biomass
		g/L			Total	Acetic	Propionic	Butyric		
Saccharina latissima	150	39.02	15.55	0.19	257.11	212.20	8.91	0.00	4.42	52
	200	42.90	16.83	0.27	648.30	533.08	78.16	3.80	4.62	58
	250	40.73	15.11	0.25	643.28	509.60	71.84	10.31	6.57	52
Fucus serratus	150	41.42	16.84	0.16	75.11	36.40	5.56	0.53	4.80	50
	200	37.14	14.48	0.20	818.07	689.31	67.35	13.76	4.76	44
	250	35.19	13.36	0.24	1001.45	867.35	84.21	11.56	6.74	41

COD = chemical oxygen demand. TOC = total organic carbon.

processing temperatures (200 °C-250 °C) are associated with an increased total phenol content compared to lower temperature processing (150 °C) (Parmar and Ross, 2019); as shown in Table 2.

Generally the pH of the process waters decrease with increasing HTC reaction temperature for lignocellulosic biomasses (Nakason et al., 2017; Nakason et al., 2018; Machado et al., 2018; Wang et al., 2018), whereas the pH of microalgae process waters slightly increases with increased HTC temperature (Marin-Batista et al., 2019). Table 2 shows the pH of process waters produced at 150 °C and 200 °C are similar, however this drastically increases for the process water produced at 250 °C, likely due to the increase in the solubilisation of ash into the aqueous phase (Smith and Ross, 2016).

3.2. Biomethane potential of hydrothermal products

There is a potential for multiple integration strategies between HTC and anaerobic digestion (AD), dependant on the type of hydrothermal product utilised as an AD feedstock; hydrochar, process water or maintaining the two phases together as a mixed slurry. This study investigates the potential for biomethane generation from the hydrothermal products derived from two species of macroalgae; *S. latissima* and *F. serratus* for each of these integration approaches. Fig. 1 displays the experimental biomethane potential (BMP_{ex}) of each of these hydrothermal products.

3.2.1. Hydrothermal slurries

The biomethane yields of un-treated (raw) *S. latissima* and subsequent hydrothermal slurries are shown in Fig. 1a. All hydrothermal slurries generate similar biomethane yields compared to the un-treated S. latissima (200 mL CH_4/g VS). Slurries produced at 150 °C, 200 °C and 250 °C, produce 217, 202 and 196 mL CH_4/g VS respectively. This suggests that anaerobic digestion of hydrothermal slurries produced at the temperatures tested in this study are not suitable for the valorisation of *S. latissima*, particularly at higher HTC temperatures. Lin et al. (2019) found an optimal hydrothermal pre-treatment temperature of 140 °C for *S. latissima* to enhance biomethane yields by 22.6% through optimal mannitol solubilisation. Ding et al., (2020) found hydrothermal treatment (140 °C, 20 mins) enhanced biomethane yields of *L. digitata* by 26.8%, compared to the un-treated *L. digitata* Additionally, Lin et al. (2019) found a treatment temperature of 160 °C could enhance biomethane generation, contradictory to the yield of biomethane produced from SL150-slurry in this study. Although, SL150-slurry generated 9% higher biomethane yields compared to un-treated *S. latissima*; this was not a significant difference ($p > 0.05$). However, Lin et al. (2019) and Ding et al. (2020) used a shorter hydrothermal retention time of 30 min and 20 min respectively, which may result in reduced levels of inhibitory compound formation, whilst still facilitating hydrolysis. He et al. (2014) reported that the greatest solubilisation of carbohydrate from rice straw at higher temperatures of 210 °C was observed at even lower residence times, in this case the primary objective was maximising sugar for bio-hydrogen production. Ding et al. (2017) found the optimal hydrothermal treatment temperature to enhance biomethane yields from food wastes was 140 °C, and once again, a significant reduction in biomethane yields was observed at temperatures above 200 °C. Therefore, the findings from this work agree with the reported literature that higher temperature hydrothermal processing is not recommended for enhancing biomethane generation from hydrothermal slurries although dwell time at temperature is also important. Lin et al. (2019) also found that at the higher HTC temperature of 180 °C, the biomethane yields reduced slightly and were lower than un-treated seaweed. This was suggested to be due to the formation of inhibitory compounds through Malliard reactions.

Conversely, the biomethane yields generated from FS150-slurry, FS200-slurry and FS250-slurry are all significantly higher ($p < 0.05$) than that from un-treated *F. serratus*, as shown in Fig. 1d. The FS150-slurry generates slightly higher BMP_{ex} (198 mL CH_4/g VS) compared to FS200-slurry (196 mL CH_4/g VS) and FS250-slurry (156 mL CH_4/g VS); 49%, 47% and 17% more than FS-raw. Again, the highest temperature slurry generates the least biomethane compared to the lower-temperature slurries, suggesting higher temperatures can negatively impact digestion. However, FS250-slurry still generates more biomethane compared to un-treated *F. serratus*. This highlights interspecies differences on the use of hydrothermal treatment and subsequent AD; which extends to differences between feedstocks. There is no significant difference ($p > 0.05$) in the biomethane yields generated by FS150-slurry and FS200-slurry. However, a treatment temperature of 150 °C would be more energetically viable.

3.2.2. Hydrochars

The hydrochars produced from *S. latissima* at 150 °C and 200 °C have similar methane yields; 185 mL CH_4/g VS and 163 mL CH_4/g VS respectively, both significantly higher ($p < 0.05$) than hydrochar generated at 250 °C; 28 mL CH_4/g VS. Table 1 shows an increasing theoretical biomethane potential (BMP_{th}) for the solid residues of *S. latissima* with increasing HTC treatment temperature due to the increasing carbon content. Consequentially, the BI of the solid residues decreases with increasing HTC temperature; 41%, 34%, 27% and 4% respectively. Table 1 shows an increasing C:N ratio of the hydrochars with increasing HTC processing temperature towards the optimal of 25–30:1 (Ward et al., 2008), suggesting an improvement in the quality of the feedstock for biomethane generation. However, the reduction in BI suggests a higher degree of recalcitrance for the hydrochars at higher temperatures and the carbon fraction available to the microbial consortia is reduced. This corresponds to higher level of fixed carbon in the higher temperature hydrochars; shown in Table 1. Mumme et al. (2014) found 10.4% of the labile carbon of hydrochar derived from wheat straw digestate, produced at 230 °C was bioavailable to contribute towards biomethane production. The biodegradability of the higher temperature hydrochar found in this study was similar to that found by Mumme et al. (2014). This is significantly lower than the biodegradability found across conventionally-used AD feedstocks (Labatut et al., 2011). Luz et al. (2018) also found biodegradability of spent-coffee ground hydrochars decreases with increasing HTC processing temperature. However, methane yields and BI of the coffee ground

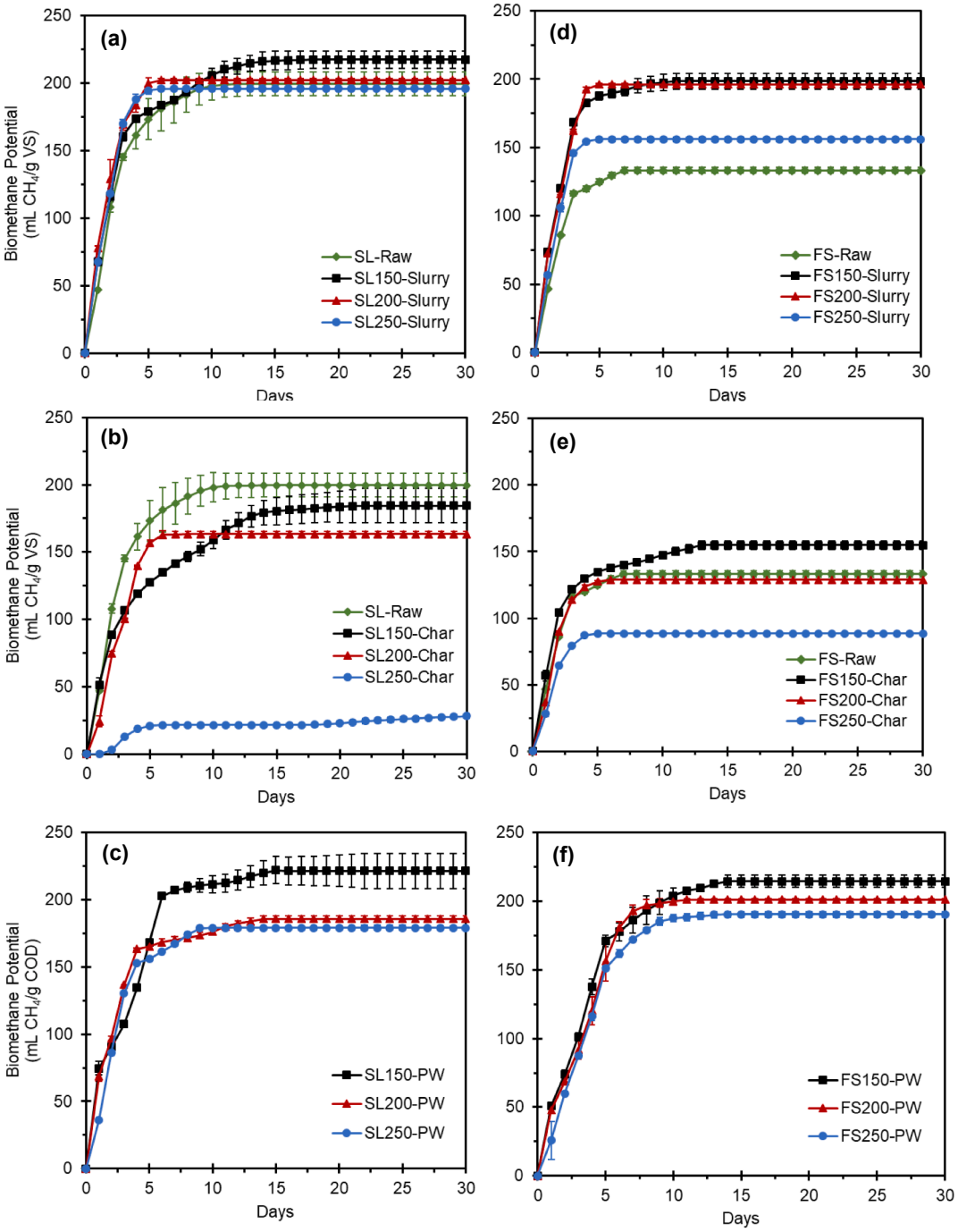

Fig. 1. Biomethane Potential of the products from the HTC of S. latissima (SL) and F. serratus (FS). Including (a) SL slurries, (b) SL chars, (c) SL process waters, (d) FS slurries, (e) FS chars and (f) FS process waters. Values are displayed as means with standard deviations shown as error bars.

hydrochars are significantly higher than those found in this study; suggesting feedstock variation. SL200 and SL250 hydrochars generate significantly ($p < 0.05$) less biomethane compared to the un-treated *S. latissima*.

Fig. 1e displays the biomethane yields of un-treated *F. serratus* and resultant hydrochars. The hydrochar generated at 150 °C generates significantly higher biomethane yields (155 mL CH_4/g VS) compared to hydrochars produced at the higher processing temperatures (200 °C and 250 °C), with FS250-char generating the least 89 mL CH_4/g VS. Therefore, as with the *S. latissima* hydrochars, *F. serratus* hydrochars decrease in BI with increasing HTC temperature; 28%, 20% and 12%. FS150-char is the only hydrochar, of all hydrochars tested, to generate a higher (16%) biomethane yield compared to the un-treated seaweed, suggesting the use of hydrochars as a feedstock for anaerobic digestion is not the most effective use of this product stream, particularly at higher temperature. Hydrochars have been proposed as an additive within anaerobic digesters to act as a support platform to facilitate microbial growth and interactions through the formation of biofilms (Mumme et al., 2014) and acting as an exchange service for metabolic products and direct interspecies electron transfer (Zhao et al., 2018). Again, this mechanism is likely to be feedstock dependent.

3.2.3. Process waters

A third integration approach is to separate hydrochar and the

process waters for alternative applications; the use of hydrochar as either a functional material (Fang et al., 2018) or a solid fuel (Smith and Ross, 2016) and the treatment of the process water for biomethane generation (Paul and Dutta, 2018). For the purposes of this study, it is suggested that the hydrochar is utilised as a solid combustion fuel due its higher calorific value (Table 1) and reduction in slagging and fouling propensity, due to the removal of alkali metals and chlorinated compounds (Smith and Ross, 2016).

The BMP_{ex} of the process waters produced from the different seaweeds is shown in Fig. 1c and 1f. The lower temperature (150 °C) process water generates significantly ($p < 0.05$) higher levels of biomethane compared to the process waters generated at 200 °C and 250 °C across both species of seaweed. The highest biomethane yields from the process waters is generated by *S. latissima* at 150 °C (222 mL CH_4/g COD). This species of seaweed is known to contain high levels of carbohydrate content (Lin et al., 2019). There is no significant difference in biomethane yields from the process waters produced at 200 °C and 250 °C for both S. latissima and F. serratus ($p > 0.05$). Wang et al. (2019) found HTC process water, produced at 220 °C from a *Laminaria* species generated 186 mL CH_4/g COD; similar to higher temperature (200 °C and 250 °C) process waters from *S. latissima*; another kelp species. Biomethane generation from kelp HTC process waters can be further enhanced by process water recirculation during HTC, due to the accumulation of VFAs (Wang et al., 2019), however, this is beyond the scope of this study. Previous studies from orange pomace (Erdogan et al., 2015) and microalgae (Marin-Batista et al., 2019) have found a decrease in the biomethane yields from the process waters with increasing HTC processing temperature. Pre-treatment strategies which facilitate hydrolysis have been found to release phenols, furfural, furfuryl alcohol, 5-HMF, formic acid, acetic acid and propionic acid (Elbeshbishy et al., 2017), which can negatively affect biodegradability of a substrate (Nakason et al., 2017; Lin et al., 2019), particularly as the severity of the pre-treatment increases. Table 2 shows both SL200 and SL250 aqueous phases contain similar levels of digestible VFAs and inhibitory phenols. This is the justification given by Lin et al. (2019) for anaerobically digesting lower-temperature hydrothermal slurries. Phenolic compounds are believed to alter the selective permeability of microbial cell membranes causing cell disruption and termination of essential enzymatic pathways (Monlau et al., 2014). Milledge et al. (2019) have previously displayed the inhibitory effects of brown seaweed-derived phenols; phloroglucinol and epicatechin during anaerobic digestion. Elbeshbishy et al. (2017) report a phenol concentration of 250–1000 mg/L can significantly inhibit mixed cultures of inoculum. Table 2 shows an increase in the total phenol (TP) content of process waters produced is between 190 and 270 mg/L. Table 2 shows process waters produced at 200–250 °C have higher concentrations of VFAs and inhibitory phenols compared to the process waters produced at 150 °C. They may also contain higher levels of soluble humins produced from polymerisation of carbohydrates fractions. Although the presence of these phenols may reduce biomethane yields from the higher temperature process waters, the concentration is towards the lower range suggested by Elbeshbishy et al. (2017) to cause inhibition. The concentration not high enough to totally inhibit the digestion process and significant levels of biomethane can still be recovered.

3.3. Energy output

Fig. 2a and 2b shows the energy output yield from the combustion of the hydrochar, biomethane generation from the process waters and a combined energetic output for *S. latissima* and *F. serratus*, following HTC, based on an input of 1 kg of dry feedstock, compared to the energy output from anaerobic digestion of the un-treated seaweed. The energetic output from the combustion of the un-treated seaweeds is not considered due to the high propensity of seaweeds to slag, foul and corrode during combustion (Ross et al., 2008; Smith and Ross, 2016). Across both seaweed species hydrothermally treated samples yield a

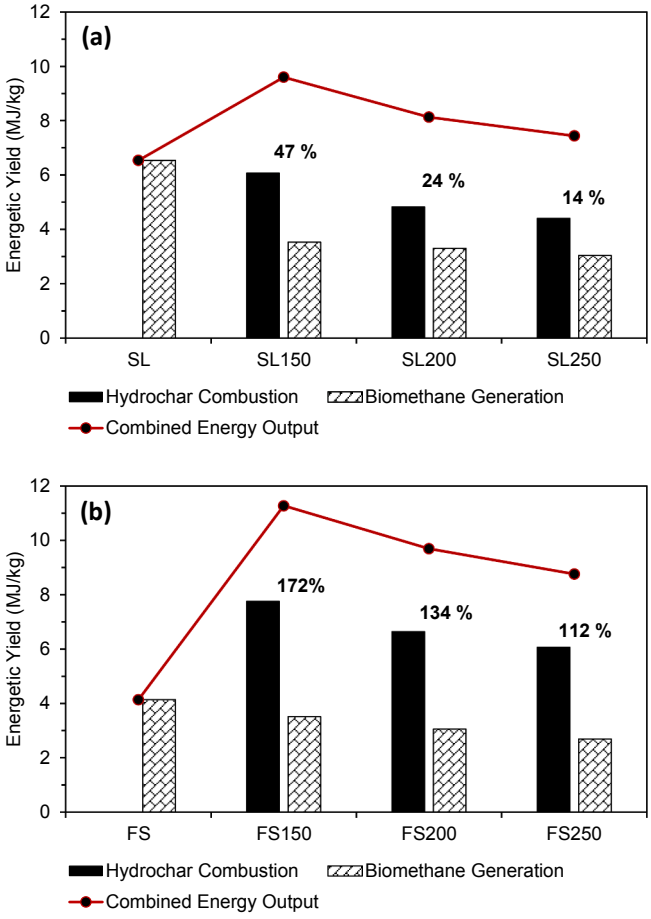

Fig. 2. Energy Output of Hydrothermal Products of (a) Saccharina latissima (b) Fucus serratus. Including energy yield from combustion of hydrochar, biomethane generation from the process waters and combined energy output. Based on 1 kg of dry feedstock. The percentage above the bars represent the total energetic output increase compared to anaerobic digestion of the un-treated seaweed.

greater energetic yield compared to the un-treated seaweed. However, there is a reduction in energy yield for both hydrochar combustion and process water anaerobic digestion with increasing HTC treatment temperature. Although increasing HTC severity leads to the formation hydrochars with a greater HHV, the hydrochar yields also significantly reduce, as shown in Table 1. This trade-off means the overall energetic output from the hydrochars are reduced at higher temperatures. Additionally, the process waters at higher temperatures also generate less biomethane than the process waters generated at lower temperatures; shown in Fig. 1c and 1f. Therefore, treating macroalgae at lower temperatures (150 °C) allows for maximum energetic output, but also reduces the energetic input of maintaining HTC at a high temperature. Similar conclusions were found by Marin-Batista et al. (2019) using similar valorisation techniques on microalgae.

Smith and Ross, (2016) predicted the theoretical biomethane yields from HTC process waters of *A. esculenta*, *L. digitata* and *L. hyperborea*, the latter across a range of seasons. Across all seaweeds analysed, the average the energetic output of methane from the process waters was 4.4 MJ/kg produced at 200 °C and 4.5 MJ/kg produced at 250 °C, based on 1 kg of feedstock. These predictions are significantly higher than found in this study from the process water produced at 200 °C; SL200 (3.3 MJ/kg), FS200 (3.1 MJ/kg), SL250 (3.0 MJ/kg) and FS250 (2.7 MJ/kg). This highlights the nature of theoretical predictions to enhance biomethane yields, due to un-predictable biodegradability during lab-scale digestions. The higher predicted average energetic

output value for process waters generated at 250 °C compared to 200 °C by Smith and Ross, (2016) suggests limitations with predicting theoretical biomethane yields, as the prediction cannot account for the effect of inhibitory compound formation.

HTC of *S. latissima* at 150 °C improves energetic yields by 47% compared to un-treated *S. latissima*. Lin et al. (2019) found hydrothermally treating *S. latissima* slurry at 140 °C improved energy output from a 2-stage digestion by 22.6%. Therefore, suggesting a significantly higher energetic return from the separation of HTC products and integrating combustion of the hydrochar and digestion of the process waters. Higher processing temperatures (250 °C) result in a significantly lower energetic return (7.44 MJ/kg), compared to HTC treatment at 200 °C (8.13 MJ/kg) and 150 °C (9.60 MJ/kg). This suggests that integration of hydrothermal carbonisation and anaerobic digestion of macroalgae at higher temperatures is not a feasible option. Therefore, for this feedstock, this study suggests the recommended option for integration is to hydrothermally carbonise macroalgae at lower temperatures, combust the hydrochar and anaerobically digest the process water, rather than anaerobically digest a hydrothermal slurry.

Fig. 2b shows the energetic output of hydrothermally treated *F. serratus* is significantly higher than that of *S. latissima* compared to their respective un-treated seaweeds. This highlights the significance of interspecies differences, suggesting this method of valorisation may be better suited to selected feedstocks. Typically, *F. serratus* is a seaweed that does not digest well within anaerobic digestion, compared to *S. latissima*. Fig. 1 shows un-treated *S. latissima* generates 50% more methane than un-treated *F. serratus*. Allen et al. (2015) report a methane yield of 342 L CH_4/kg VS for *S. latissima* and 102 L CH_4/kg VS for *F. serratus* the respective highest and lowest BMP of the ten Irish seaweeds tested in that trial. The authors suggest this is due to a low C:N of 15.5. However, in this study, both *S. latissima* and *F. serratus* have a similar C:N (17.4–17.8); shown in Table 1. Vanegas and Bartlett, (2013) again found *F. serratus* to have the lowest biogas yields of six Irish seaweeds; 65 mL biogas/g VS; 73% less than *S. latissima*; the authors conclude *F .serratus* is un-suitable for digestion. This study found *F. serratus* treated at 150 °C increases energetic output by 172%, with the combined energy output of hydrothermally-treated *F. serratus* consistently higher than *S. latissima* across all hydrothermal treatment temperatures, despite the energy recovered from digestion of the process waters being similar across both species of seaweed. Combustion of the hydrochars offers a greater energetic output compared to digestion of the process waters across all HTC temperatures and seaweed species, despite Table 2 showing almost equal sequestering of carbon between the hydrochar and process water. Therefore, the hydrochar is a greater energetic carrier compared to the process waters following HTC. Marin-Batista et al. (2019) found similar results for microalgae at temperatures of 210 °C and 240 °C. However, at the lower HTC temperature 180 °C the energetic yield of biomethane from the process water surpassed that of the hydrochar. Fig. 2b shows a greater energetic output from the FS hydrochars compared to the SL hydrochars (Fig. 2a) across all HTC temperatures. Table 1 shows FS hydrochars have a greater HHV as well as greater hydrochar yields compared to SL, explaining the greater energetic output.

Smith and Ross, (2016) and Kantarli et al. (2019) found an increasing HTC processing temperature improved the quality of the hydrochar from macroalgae; improving both the calorific value and ash chemistry properties. HTC processing temperatures of both 200 °C and 250 °C reduced the slagging and fouling capacity of macroalgae hydrochars through the solubilisation of problematic inorganics; such as alkali salts, into the process water (Smith and Ross, 2016). However, Smith and Ross. (2016) did not investigate the influence of HTC at 150 °C on hydrochar properties as a combustion fuel; calorific value and removal of inorganics. Literature suggests hydrothermal treatments below 160–180 °C do not significantly disrupt the major biochemical components of biomass (Luz et al., 2018; Liu and Balasubramanian, 2014), suggesting true carbonisation cannot occur at 150 °C. Therefore, a hydrochar produced at 150 °C may not possess all the enhanced properties as a combustion fuel as hydrochars produced at higher temperatures (200 °C and 250 °C). However, Table 1 shows a hydrochar yield of 37.5% (SL150-char) and 44.7% (FS150-char); shown in Table 1 and high concentrations of COD and TOC in SL150-PW and FS150-PW suggests a high degree of hydrolysis at 150 °C. Additionally, Table 1 shows an ED of 1.36 and 1.27 for SL150-char and FS150-char respectively, suggesting energy densification reactions are still occurring at 150 °C. Additionally, Fig. 3 displays the removal efficiencies of inorganic elements from hydrochars, compared to an un-treated sample of *L. digitata* (collected from Clachan Sand, Scotland UK in 2009); another typical seaweed found in the UK. The samples were processed through the same HTC process detailed in Section 2.2. Sodium removal efficiency was lower for 150 °C chars (63%) compared to 200 °C and 250 °C chars (100%). However, 63% still represents a significant removal of sodium and it is possible this could be removed further on washing. Removal of Potassium, chlorine and sulphur were similar for each temperature reaching over 80% reduction. At higher temperature, there is a slight reduction in sulphur removal. Therefore, Fig. 3 suggests that a significant reduction of inorganics is observed even at 150 °C, which is one of the key barriers to using macroalgae as a solid fuel. This reduction will significantly reduce its slagging and fouling tendencies, as described in Smith and Ross, (2016). This, in combination with the energy densification described in Table 1 suggests macroalgae processed at 150 °C could still be used as a viable solid combustion fuel.

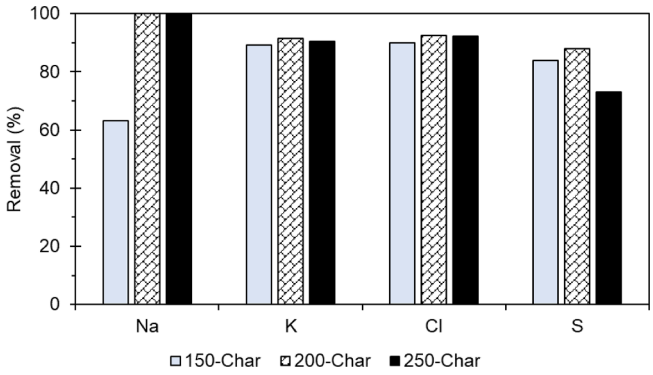

Fig. 3. Removal efficiency (%) of inorganic elements compared to the un-processed Laminaria species.

3.4. Energy balance

Accounting for a complete net energy balance, Table 3 displays the energy input required for the HTC reaction based on a starting point of 1 kg dried seaweed. The energy output is based upon the energy recovered from the combustion of the hydrochar and biomethane generation from the process waters. Additionally, the energy return on

Table 3
Net energy balance for the integration of HTC and AD based on starting with 1 kg of dried seaweed. Energy input is based on the energy required for the HTC reaction. Energy output is based on the combustion of hydrochar and anaerobic digestion of the process water.

Seaweed	HTC Processing Temperature (°C)	Energy Input (MJ/kg)	Energy Output (MJ/kg)	Net Energy Balance[1](MJ/kg)	EROI[1]
S. latissima	150	5.44	9.60	8.78	11.76
	200	7.61	8.13	6.99	7.12
	250	9.79	7.44	5.97	5.07
F. serratus	150	5.44	11.28	10.46	13.82
	200	7.61	9.69	8.55	8.49
	250	9.79	8.76	7.29	5.97

[1] Assuming a heat recovery efficiency of 85%. EROI = energy return on energy invested.

energy invested (EROI) and net energy balance is calculated, with the assumption of 85% heat recovery efficiency (Yuan et al., 2019). Both seaweed species show a similar trend; with the highest EROI at a HTC temperature of 150 °C and a decrease in EROI with increasing HTC temperature. This is linked to the increased energy requirement to heat the HTC reactor, coupled with a reduction in the biomethane yields generated from the process waters and a reduction in the yields of hydrochar; therefore, significantly less material is available for combustion. FS shows a greater EROI compared to SL across all HTC processing temperatures. FS150 offers the greatest EROI of 13.82 therefore, this method of macroalgae valorisation could be a potential route for utilising under-utilised or under-performing species, such as *F. serratus* into a practical material for a sustainable bioeconomy.

4. Conclusions

The integration of hydrothermal carbonisation (HTC) and anaerobic digestion (AD) is a potential valorisation route for the use of macroalgae as a feedstock for bioenergy generation. The most energetically feasible integration route is observed for utilisation of the hydrochars as a solid fuel and generating biomethane from the process waters. HTC treatment at 150 °C represents the greatest increase in energetic output; 47% and 172% respectively for *S. latissima* and *F. serratus*, based on this valorisation route.

CRediT authorship contribution statement

Aaron E. Brown: Conceptualization, Investigation, Data curation, Formal analysis, Methodology, Project administration, Resources, Software, Validation, Visualization, Writing - original draft, Writing - review & editing. **Gillian L. Finnerty:** Conceptualization, Formal analysis, Investigation, Methodology, Project administration, Resources. **Miller Alonso Camargo-Valero:** Conceptualization, Funding acquisition, Investigation, Project administration, Resources, Supervision, Validation, Visualization, Writing - review & editing. **Andrew B. Ross:** Conceptualization, Funding acquisition, Investigation, Project administration, Resources, Supervision, Validation, Visualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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