Thermo-catalytic reforming pyrolysis of ensiled *Saccharina latissima* dominated macroalgal pellets for bioenergy production

Marie E. Kirby [a],[*], Trisha Toop [a], Miloud Ouadi [b], Lesley McEvoy [c], Christine Rolin [c], Rhiannon Inkster [c], Philip W. Dyer [d], Michael K. Theodorou [a]

[a] *Agriculture and the Environment Department, Harper Adams University, Newport, Shropshire TF10 8NB, UK*
[b] *School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK*
[c] *NAFC Marine Centre (UHI), Port Arthur, Scalloway, Shetland, ZE1 0UN, UK*
[d] *Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK*

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ABSTRACT

Marine macroalgae is a biomass resource for the manufacture of fuels and chemicals, which can be sustainably harvested from seaweed farms or from man-made structures where it accumulates as a biofouling organism. However, in temperate regions farmed macroalgae can only be harvested between late Spring and early Summer, limiting year-round availability. Here we show that a conventional grass ensilage procedure preserves *Saccharina latissima* dominated biomass on the tonne scale for 30 months, enabling year-round use of this biomass. Following processing, the resulting dried and pelletised ensiled macroalgae material was subject to Thermo-Catalytic Reforming™, comprising sequential pyrolysis (450 °C) and either dry or steam catalytic reforming (700 °C) processes. Both processing methods produced a mixture of bio-oil (1.6–1.9 wt%) and hydrogen-rich permanent gases (30.9–31.1 wt%) with higher heating values of 34.8–35.4 MJ/kg and 18.0–24.2 MJ/m³, respectively, together with char (45.5–48.5 % wt). The permanent gases can be used directly for heat generation, while hydro-treatment of the bio-oil would afford a material that can be blended with traditional transport fuels. This work demonstrates that if operated at scale, the combined harvesting, ensilaging and Thermo-Catalytic Reforming™ of preserved macroalgal biomass offers a year-round decentralised energy resource.

Introduction

The use of marine macroalgae (seaweed) as a substantial biomass resource to produce sustainable energy vectors is currently in its infancy [1,2]. The combination of greater photosynthetic efficiency of macroalgae (~7%) compared with terrestrial plants (~2%) [3], coupled with greater production yields (for example brown algae range of the order of up to 60 tonnes dry matter/hectare/year [4], maize (17 tonnes dry matter/hectare [5]) and wheat (~18 tonnes dry matter/hectare [6])), no requirement for fresh water and agricultural land [4] offer significant advantages in terms of biomass to energy conversion. What is more, macroalgae can be readily converted to desirable "drop-in" non-fossil-derived energy vectors (bio-oil and hydrogen-rich permanents gases) using a number of established pyrolysis methods [2,7–9].

Commercially, macroalgae is mainly harvested from wild stocks or grown in aquaculture systems at sea or in land-based tanks. Less commonly, but equally importantly, macroalgae can also be harvested as a by-product of other industries, for example from offshore wind turbines, and fish or mussel farming. Globally in 2020, 36 million tonnes (fresh weight) of macroalgae were harvested, of which 97 % was from aquaculture [10]. Asia accounts for 97 % of global macroalgae production [10]. In Europe and the UK, brown kelp, e.g., *Saccharina latissima*, *Laminaria digitata* and *Alaria esculenta* are farmed and commonly found as biofouling organisms. These large, fast-growing kelp thrive in temperate oceans, which creates a unique opportunity in Europe for biomass production for fuel [4,11] and hence are an attractive sustainable energy resource [12–14].

There are several limitations to the application of macroalgae as a feedstock. Firstly, its high moisture content dictates dewatering prior to processing [15]. Although a range of thermal, chemical and mechanical

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drying methods have been explored, each suffer from significant limitations [16–20]and are adversely impacted by seasonal changes in composition [19]. Secondly, the relatively narrow seasonal harvesting window, especially in temperate regions, of late Spring to early Summer, significantly limits availability. This constraint dictates that for macroalgae to be used as a secure, year-round biomass resource, a reliable storage and/or preservation methodology is required [16]. Seaweed decomposition prior to processing leads to both loss of energy content and to environmental issues with liberation of noxious gaseous degradation products [17].

At a laboratory scale, one of the most promising macroalgal preservation methods is ensiling, a process that is ubiquitous, cheap and simple for the preservation of terrestrial agricultural feedstocks, for example grasses and maize. Ensiling involves epiphytic bacterial conversion of residual sugars in the harvested crop organic acids, mainly lactic acid, in an anoxic environment, thereby reducing the biomass' pH and inhibiting further microbial degradation [19–26]. In this work we demonstrate for the first time, the successful ensiling of seasonally harvested *S. latissimi* dominated macroalgae in semi-commercial tonne-scale for year-round storage. Subsequently, we show that combined pyrolysis/catalytic reforming (so-called Thermo-Catalytic Reforming, TCR [27,28]) of the resulting ensiled macroalgae delivers both a liquid bio-derived fuel grade material and hydrogen-rich permanent gas stream, two key sustainable liquid and gaseous energy vectors or feedstocks for chemicals manufacture. Use of post-pyrolysis reforming produces bio-oils and permanent gas streams of superior quality, high energy densities and decreased oxygen contents and hence greater stability, compared to other direct pyrolysis-derived biofuels [29], that could provide year-round biofuels to decentralised communities.

Materials and methods

Collection of macroalgae

Mixed brown macroalgae naturally growing as a biofouling organism on farmed mussel lines were harvested in June off the east coast of Trondra (latitude and longitude of 60°07.119′N, 001°16.456′W), Shetland. From visual inspection, the harvested seaweed was dominated by *S. latissima* (approximately 90–95 %), but also included some *L. digitata*

and *Sacchoriza polyschides* (Fig. 1). The mussel lines were set with 10 m droppers and raised out of the sea to harvest the macroalgae (the whole plant was harvested by hand-cutting at the stipe). Approximately one metric tonne of macroalgae was collected and brought ashore. The harvesting process was completed within three hours.

Preparation and storage of macroalgal silage and production of ensiled macroalgal pellets

Once onshore, the macroalgae were spread out onto stacking trays with drainage holes and left to drain overnight at room temperature with natural ventilation. The following day, the macroalgae were chopped (to approximately 3 × 2 cm, length × width) with a Viking GE-250 garden shredder (STIHL, UK). Ten-kilogram batches of chopped macroalgae were placed into a 136 L capacity Belle Minimix 150 electric concrete mixer (Belle Engineering Ltd, UK) and mixed for 10 min with a conventional salt-based silage preservative, "Safesil" (Salinity, UK) applied at a loading of 4 L/tonne of fresh macroalgae with a fine nozzle watering can. On completion, the treated macroalgae were removed and placed into a large 69 L plastic Tuff light-tight bucket (Curver, UK) lined with a 914 × 1219 mm heavy-duty polythene bag (Kite Packaging, UK). A total of 50 kg of macroalgae were added to each container, prior to minimising the airspace through compaction and sealing the bag with black pvc silage tape (100 mm × 33 mm; Sticky Products, Markham, UK). The top of each container was weighted with 10 kg of dry sand. A total of 14 containers were prepared; these were stored at room temperature (~15 °C) for 30 months, before the bags were opened and effluent removed (Table 1). The ensiled macroalgae were oven dried at 90 °C for 4 h (Universal Oven UF750, Memmert, Germany) to 12 % moisture content (MA35, Sartorius moisture meter, Germany). After drying, the ensiled macroalgae were pelleted (6 mm diameter by 23 mm length) using a PK series flat die pelletiser (Leabon, China) with a 70 kg/hour throughput.

Ensiled macroalgae pyrolysis

Pyrolysis was undertaken using a TCR-2 bench scale auger reactor as described by Ouadi et al. [29] and Ahmed et al. [8], with TCR design diagrams are available from Kirby et al., [30] (Fig. 2). This system has a

Fig. 1. Extracted mussel line prior to harvesting, dominated by *S. latissima* (approximately 90–95%), including some *L. digitata* and *Sacchoriza polyschides*. The red and green seaweeds visible on the mussel line were discarded and not used in this research. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Individual container *Saccharina latissima* dominated silage and effluent pH values and effluent volumes (kg and %).

Container number	Ensiled *Saccharina latissima* dominated silage pH	Total effluent (kg) and (as a percentage of fresh weight)	Effluent pH
1	4.8	25.1 (49.4)	4.4
2	4.2	11.2 (21.8)	4.0
3	4.5	10.2 (21.0)	4.1
4	4.5	4.4 (11.5)	4.6
5	4.1	4.9 (11.0)	4.3
6	4.2	11.6 (23.7)	4.4
7	4.1	12.4 (23.3)	4.0
8	5.4	26.2 (56.1)	4.6
9	4.2	11.0 (23.0)	4.4
10	4.2	11.5 (24.7)	4.3
11	4.1	11.7 (24.7)	4.2
12	4.2	15.1 (30.5)	4.2

N.B. Weights of each container upon opening ranged from 38.8–53.2 kg and these were used in calculating the total effluent weight percentage.

processing rate of 2 kg/hour. The first stage of the TCR-2 reactor was preheated to 450 °C (in line with intermediate pyrolysis conditions) and the post-pyrolysis reformer preheated to 700 °C and the system allowed to stabilise for 90 min prior to the addition of pelleted ensiled *S. latissima* dominated silage via the rotating auger (6.42 rpm). The whole system was continuously purged with nitrogen to remove any oxygen and was operated at 100 mbar overpressure. For each experimental run, 6 kg of macroalgal pellets were pyrolysed at a rate of ~1 kg/hour, with a total solid residence time in the heated auger reactor of 5–10 min. The resulting primary products from the pyrolyser unit (biochar, volatile gases and vapours) were fed directly into the catalytic post-pyrolysis reformer stage held at a higher temperature of 700 °C, where biochar accumulates. Over time the biochar develops into a fixed-bed catalytic reactor through which the volatile pyrolysis products are forced. This biochar bed mediates catalytic cracking, which increases the yield of permanent gases, carbon monoxide and hydrogen [28,31]. Two different TCR methods, with and without (dry) stream reforming, were performed to determine optimal conditions for converting the pyrolysed ensiled *S. latissima* dominated macroalgal pellets to different energy vectors. In the TCR-steam treatment experiment, water was added to the feedstock (5 % weight basis) prior to pyrolysis to enable steam reforming to occur at the post-pyrolysis reformer.

Chemical analyses of algal biomass and pyrolysis products

The pH of the algal biomass before and after ensiling and storage was determined by taking a 10 g sample of each material into a Stomacher bag with 90 ml of deionised water. The sample was pummelled using a Seward Stomacher 400 Circulator (Seward Ltd, Worthing, UK) for 3 min at 230 rpm. The pH of the resultant material was determined using a calibrated, combination pH probe (Jenway 3505 pH Meter; Jenway, UK).

Chemical analyses were undertaken on the ensiled pelleted macro-algal material and the pyrolysis products: char, bio-oil, aqueous and permanent gases. After each experiment, the bio-oil and aqueous phase materials produced from the TCR reactor were phase separated using a standard glass separating funnel under gravity and the two fractions collected separately. Moisture (all samples) and ash (ensiled, dried macroalgae and char) contents were determined using a Philips K5 94 muffle furnace applying standard American Society for Testing and Materials (ASTM) E1756-08 [32] and ASTM E1755-01 [33] methods, respectively. The ash content of the bio-oil was calculated in accordance with ASTM D482-13[34]. All samples were analysed for carbon, hydrogen, nitrogen and sulfur, with oxygen being determined by difference, by MEDAC Ltd, Cobham, UK. The carbon, hydrogen, nitrogen analyses were determined according to ASTM E777-17a [35] and ASTM E778-15 [36], respectively. Sulfur content was measured according to ASTM E775-15 [37]. The higher heating value (HHV) of all samples were determined using the unified correlation for fuels method developed by Channiwala and Parikh [38], based on the relative composition of each sample (carbon weight fraction, hydrogen, sulfur, oxygen, nitrogen and ash content).

Bio-oil moisture content was determined using a Karl Fischer V30 compact volumetric titrator (Mettler Toledo, UK) in accordance with ASTM E203-01 [39]. The result was corrected to weight percentage of the total sample. The total acid number (TAN) of the bio-oils was determined with a Mettler Toledo V20 compact titrator (Mettler Toledo, UK), using the potentiometric titration method in accordance with ASTM D664-18e2 [40]. Bio-oil kinetic viscosities were determined in accordance with ASTM D445-06 [41]. Chemical composition of the bio-oils were probed by GC–MS, which was performed using a 7820A Agilent HP gas chromatograph connected to a 5977E Agilent HP quadrupole mass spectrometer (EI 70 eV, at a frequency of 1.55 scan/s within the 29–300 *m/z* range). Analytes were separated by a DB-FFAP nitro-terephthalic acid-modified polyethylene glycol column (30 m, 0.25 mm i.d., 0.2 μm film thickness) using helium as a carrier gas with the following thermal program: 50 °C with a hold for 5 min; then ramping
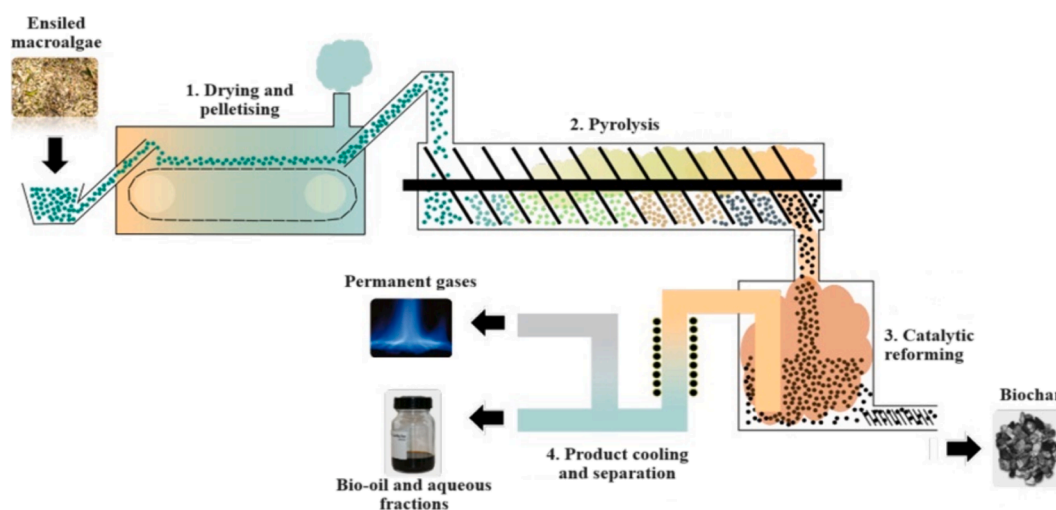

Fig. 2. Schematic of the Thermo-Catalytic Reforming (TCR) process.
Source: modified from [30]

up with a heating rate of 10 °C/min until 250 °C; followed by column cleaning at 250 °C for 10 min. A sample of bio-oil was dissolved in acetonitrile solution to a 1 % (w/v concentration), spiked with 0.1 ml internal standard solution (1000 mg/l, 2-ethyl butyric acid in acetonitrile). The compounds were identified by comparison with library searches (NIST 17 libraries) and mass spectra evaluation of peaks were quantified in terms of relative abundance (percentage peak area to the total area).

The permanent gases were measured directly at the outlet from the TCR reactor using a Pollutek GAS 3100P Syngas analyser calibrated for detection of hydrogen, methane, carbon monoxide, carbon dioxide and hydrocarbons, via NDIR and TCD detectors with automatic online gas calorific value determination. The mass and energy balances were calculated based on the relative mass (wt%) or energy content of each individual pyrolysis product respectively, compared to all pyrolysis products.

Results and discussion

Chemical characteristics of ensiled S. latissima dominated macroalgae

The pH of the macroalgae seaweed prior to ensiling was 6.8. Each of the 14 prepared 50 kg containers were opened at the end of the 30-month period; two of them had mould growth (presumed to result from significant air ingress) and being non-representative, were not included in further research. The pH of the ensiled macroalgae in the remaining 12 containers was recorded and found that the pH in 11 of the containers declined during the ensilage process reaching an end-point range of 4.1–4.8 (Table 1). In the remaining container, number 8, the macroalgal silage had a slightly higher end-point pH of 5.4 (Table 1), something attributed to a small amount of air ingress that partly inhibited the ensiling process. During the storage period nine of the containers produced a quantity of silage effluent in the range 11.0–24.7 wt%, while three containers produced considerably higher effluent volumes of 30.5, 49.4 and 56.1 wt% (Table 1). The silage effluent volumes of 11.0–24.7 wt% were similar to those previously published for ensiling of *S. latissima* of 10–18 % [22]. The higher effluent yields produced by three of the containers have been attributed to slow air ingress into the container leading to a small degree of fungal growth or longer-term clostridial growth, both of which can contribute to increased effluent production and macroalgae degradation [42]. The pH of liquid effluent drained from all of the containers at the end of the storage period ranged from 4.0 to 4.6 (Table 1). The pH ranges of the ensiled *S. latissima* dominated silage were similar to the pH ranges for *S. latissima* noted by Herrmann et al., [22] who demonstrated slightly lower pH at 90 days of ensiling (silage 4.0, effluent approximately 3.8). The proximate and ultimate analyses for the ensiled *S. latissima*

dominated silage are summarised in Table 2 which includes a comparison of the proximate and ultimate analyses of previously published data of different non-ensiled macroalgae species. The composition of ensiled *S. latissima* dominated silage had lower carbon and hydrogen concentrations, and higher ash content to those determined previously for other non-ensiled macroalgae. This was due to loss of carbon through generation of carbon dioxide (the product of mixed acid fermentation) and loss of carbon into the silage effluent during the ensiling process and the degradation of organic material generating hydrogen ions in the silage effluent to reduce the biomass' pH. The concentration of ash fraction within the ensiled biomass increased, due to fermentation losses including carbon lost through silage effluent and carbon dioxide to atmosphere, leading to a reduced HHV compared to that of other untreated macroalgae [43], reducing the potential of *S. latissima* dominated silage as future energy carriers. The variation in proximate and ultimate analyses of macroalgae summarised in Table 2 is due to the species of macroalgae analysed, seasonal variation and any pre-processing methodologies applied [43,44]. Compared to terrestrial biomass, pyrolysis of macroalgal biomass leads to higher ash concentrations (35 % compared to grass of 5–8 %) [45], a lower carbon:oxygen ratio (0.87 compared to that of grass) and lower HHV (10.0 MJ/kg compared to grass of 17–18 MJ/kg [46]and paper pulp of 22.9 MJ/kg [29].

TCR products obtained from ensiled S. Latissima dominated macroalgal pellets

The pyrolysis products obtained using TCR-dry (without steam reforming) and TCR-steam (with steam reforming) of ensiled *S. latissima* dominated macroalgal pellets, quantified by mass (wt%) and liberated energy (%) balances for each of the four pyrolysis products (bio-oil, permanent gases, char and aqueous fraction) are summarised in Table 3. Differences between the products obtained using TCR-dry and TCR-

Table 3

Pyrolysis product yields (mass and energy basis) from ensiled *Saccharina latissima* dominated macroalgal pellets produced with the Thermo-Catalytic Reforming (TCR) operated without steam reforming (TCR-dry) and with steam reforming (TCR-steam).

Pyrolysis products	Mass (wt %)		Energy balance (%)	
	TCR-dry	TCR-steam	TCR-dry	TCR-steam
Bio-oil	1.9	1.6	6.0	5.0
Permanent gases	30.9	31.3	55.0	58.0
Char	45.5	48.5	39.0	37.0
Aqueous fraction	21.7	18.6	–	–

Table 2

Comparison of relative compositional analyses of ensiled *Saccharina latissima* dominated macroalgal silage for this research, compared to non-ensiled *Laminaria digitata* and *Laminaria hyperborean* from [44] and [43].

	Ensiled *Saccharina latissima* dominated macroalgal silage	*Laminaria digitata*[a]	*Laminaria hyperborean* (summer)[a]	*Undaria pinnatifida*[b]	Acid-washed *Undaria pinnatifida*[b]
Ultimate analyses (wt%)					
Carbon	27.2	33.3	38.2	34.0	47.5
Hydrogen	3.8	4.7	5.3	5.0	5.1
Nitrogen	1.8	1.7	1.9	3.3	4.1
Sulfur	0.7	0.9	0.6	0.7	0.6
Oxygen (by difference)	31.4	31.1	33.3	57.0	42.7
Proximate analyses (wt%)					
Ash	35.1	28.3	14.5	25.8	0.8
Moisture content	12.0	–	–	–	–
Higher heating value (HHV) (MJ/kg)	10.0	12.4	20.6	7.7	17.3

N.B. Comparison data from [a] [44] and [b] [43].

steam methods were minimal, with only a slightly higher char yield and lower aqueous fraction achieved when using the TCR-steam method. For both pyrolysis methods, the char component was the largest product fraction by mass produced, followed by the permanent gases, aqueous products and a relatively small proportion of bio-oil. The mass yield of bio-oil from TCR-dry (1.9 %) and TCR-steam (1.6 %) experiments were both lower in comparison to the pyrolysis products produced from other TCR feedstocks (wheat husks, 6 % [47]; used wet wipes, 12 % [48] and residual sugar bagasse, 21 % [8]). In comparison to the TCR product mass yields obtained here (450 °C), previously reported pyrolysis of non-ensiled *Laminaria japonica* at a range of temperatures between 300 and 600 °C revealed that at the yields (wt%) of bio-oil, gas, and char fractions changes significantly 15, 32 and 54 % at 300 °C compared to 31, 28 and 38 % at 600 °C [43]. This difference in mass yields obtained between slow and intermediate pyrolysis were due to pyrolysis temperature, as the char yield reduces as temperature increases, whilst bio-oil and permanent gas fractions increase [43]. Longer solid residence times at elevated temperatures can also increase catalytic cracking of higher molecular weight vapours, increasing permanent gas and reducing bio-oil yields [49]. In this research, the energy balance of both pyrolysis methods produced the greatest energy balance from the permanent gas fractions, followed by the char and then the bio-oil fractions. The HHV of the TCR-steam biochar fraction was reduced due to the increase ash content (Table 3).

Production of bio-oil from ensiled S. Latissima dominated macroalgal pellets

There are a range of specific fuel properties and specifications required for a drop-in liquid biofuel, for example bio-oil, to be suitable for use. Bio-oil fuels used for engine applications require low oxygen contents, as biofuels with high oxygen contents are harder to combust, have reduced stability during storage (due to polymerisation) and reduced calorific value [27]. The oxygen content of bio-oils from different pyrolysed feedstocks can vary over a considerable range, from relatively low values of ~6 % for pyrolysed municipal solid waste (MSW) to much higher values of ~30 % for pyrolysed wheat husks [47,50]. Both the bio-oils produced in this study had relatively low oxygen contents (8.0 %, TCR-dry and 6.6 %, TCR-steam), values that are comparable to commercial biodiesel, which has an oxygen content of 9.4 %[27]. Additionally, the ultimate analyses of the TCR-dry and TCR-steam bio-oils obtained here show that the TCR-steam treatment produces a bio-oil with a slightly higher carbon content and lower hydrogen, sulfur and oxygen contents (nitrogen remained unchanged) compared to the TCR-dry treatment (Table 4). Together, these data demonstrate that TCR-processed ensiled *S. latissima* dominated macroalgal pellets can produce bio-oils suitable for use as a blend component with other engine fuels.

Processing of ensiled *S. latissima* dominated macroalgal pellets using both the TCR-dry and TCR-steam methods produced a bio-oil that had a high moisture content and was of low viscosity (Table 4), compared to other feedstocks. For example, combined TCR pyrolysis of anaerobic digestates produced a bio-oil with < 2 % moisture and a viscosity of 40.0 cSt [27]. The lower viscosity of the bio-oils obtained herein is beneficial for commercial application as the biofuel is easier to pump and aids nozzle dispersion [29]. In contrast, macroalgae hydrothermal and fast pyrolysis bio-oils both require further processing before they can be used as biofuels due to their higher viscosity and nitrogen contents [51].

The TCR-steam method produces a bio-oil with a considerably reduced ash content and lower TAN in comparison to the material obtained through TCR-dry treatment (Table 4). However, both TCR methods produce a bio-oil with high ash contents (0.6 %, TCR-dry and 0.2 %, TCR-steam) in comparison to previously published data for other feedstocks (e.g., <0.001 % for wheat husks [47]; 0.2 % for anaerobic digestate [27]). The TAN content for the materials obtained from both TCR methods used here were within the lower range (9.9 mg KOH/g,

Table 4

Relative compositional analyses of bio-oil derived from ensiled *Saccharina latissima* dominated macroalgal pellets produced with the Thermo-Catalytic Reforming (TCR) operated without steam reforming (TCR-dry) and with steam reforming (TCR-steam).

	Bio-oil production method	
	TCR-dry	TCR-steam
Ultimate analyses (wt%)		
Carbon	77.9	80.5
Hydrogen	7.2	6.8
Nitrogen	5.4	5.3
Sulfur	0.9	0.6
Oxygen (difference)	8.0	6.6
Fuel properties		
Ash (wt%)	0.6	0.2
Moisture content (w/v%)	16.1	12.5
Total acid number (TAN) (mg KOH/g)	9.9	5.2
Viscosity (cSt)	21.8	9.0
Density (g/cm^3)	1.0	1.0
Higher heating value (HHV) (MJ/kg)	34.8	35.4

TCR-dry and 5.2 mg KOH/g, TCR-steam) when compared to TCR bio-oils produced from other feedstocks and much lower than that for fast pyrolysis-derived bio-oils. For example, fast pyrolysis of wood can give rise to materials with TAN values of 11–200 mg KOH/g [52]. Lower TAN values are commercially important since bio-oils with lower TAN contents cause less engine wear and corrosion [53].

The materials obtained from both the TCR-dry and TCR-steam methods have a high HHV (34.8 MJ/kg and 35.4 MJ/kg, respectively) despite the high moisture content of the bio-oils (Table 4). Notably, the values of HHV for the bio-oils produced here from TCR processing of ensiled *S. latissima* dominated silage are significantly higher than for pyrolysis bio-oils from other bio-derived feedstocks, for example wheat husks (26.0 MJ/kg, [47]), but slightly lower than the HHV of bio-oil resulting from pyrolysis of plastic-rich MSW (38.2 MJ/kg, [50]) and biodiesel (40 MJ/kg, [54]). Depending on the nature of the pyrolysis method employed, macroalgae can produce bio-oils with varying HHVs. For example, the fast pyrolysis of *Ulva lactuca* generated bio-oils with HHVs in the range 18.9–25.7 MJ/kg [55], whilst the fast pyrolysis of *Saccharina japonica* produced a bio-oil with a HHV of 33.0 MJ/kg [56]. This variation in HHV is believed to result from a complex combination of the bio-oils' chemical composition (and hence its origin) and physical properties [57].

GC analysis of the bio-oils obtained for both TCR-dry and TCR-steam methods shows these materials are comprised of many compounds, with the composition being dependent on the pyrolysis method employed. The bio-oil resulting from the TCR-dry method has a composition rich in aromatic hydrocarbons (51 %) and esters (18 %), together with a small quantity of organic acids (9 %). In contrast, the bio-oil resulting from TCR-steam treatment, has a significantly lower concentration of aromatic hydrocarbons (35 %) and shows a reversal in relative concentrations of organic acidic (14 %) versus esters (2 %).

Production of pyrolysis gases from ensiled S. Latissima dominated macroalgal pellets

As expected, the composition of the non-condensable, permanent gas fractions differed according to whether TCR-dry or TCR–steam processing was employed. The composition of the permanent gases obtained from the TCR-dry processing of the macroalgae pellets was rich in hydrogen (46.7 %) and contained significant quantities of carbon monoxide (26.0 %), carbon dioxide (13.7 %) and methane (12.7 %) (Table 5). In contrast, the composition of the permanent gases obtained using the TCR-steam method was dominated by carbon monoxide (31.7 %), accompanied by lower concentrations of hydrogen (24.6 %),

Table 5

Relative compositional analyses of permanent gases derived from ensiled *Saccharina latissima* dominated macroalgal pellets produced with the Thermo-Catalytic Reforming (TCR) operated without steam reforming (TCR-dry) and with steam reforming (TCR-steam).

Permanent gases (vol%)	Permanent gases production method	
	TCR-dry	TCR-steam
Hydrogen	46.7	24.6
Methane	12.7	22.5
Carbon monoxide	26.0	31.7
Carbon dioxide	13.7	19.3
Higher heating value (MJ/m^3)	24.2	18.0

N.B. Hydrocarbons were noted for both TCR methods (TCR-dry 0.9% and TCR-steam 1.9%).

methane (22.5 %) and carbon dioxide (19.3 %) (Table 5). Previous macroalgal pyrolysis processes have shown varied permanent gas composition profiles depending on the precise nature of the feed and

conditions employed. For example, Bae et al., [43] demonstrated the pyrolysis of fresh Laminaria macroalgal biomass at 500 °C produced predominantly carbon dioxide (approximately 70 %), followed by C_1-C_4 hydrocarbons (15 %), carbon monoxide (15 %) and hydrogen (≲5%).

The temporal pattern of permanent gas production varies according to the precise TCR method employed, although under both conditions it takes approximately 50 min for the TCR reactor to reach steady-state operating conditions (stable temperature and a sufficient biochar catalyst bed) (Fig. 3). When using a TCR-dry process, once optimal conditions are met there is rapid onset of dry methane reforming, Eq. (1), leading to a relatively constant gas product composition consisting of principally hydrogen and carbon monoxide, with low levels of carbon dioxide and methane [58]. It is assumed that the cracking process is accompanied by the reverse Boudouard reaction, Eq. (2), whereby carbon dioxide reacts with carbon from the char fraction to form carbon monoxide [53]. Analysis of the gas stream obtained under TCR-steam treatment conditions shows that gas composition evolves gradually across the duration of the experiment (200 min) (Fig. 3b). While the
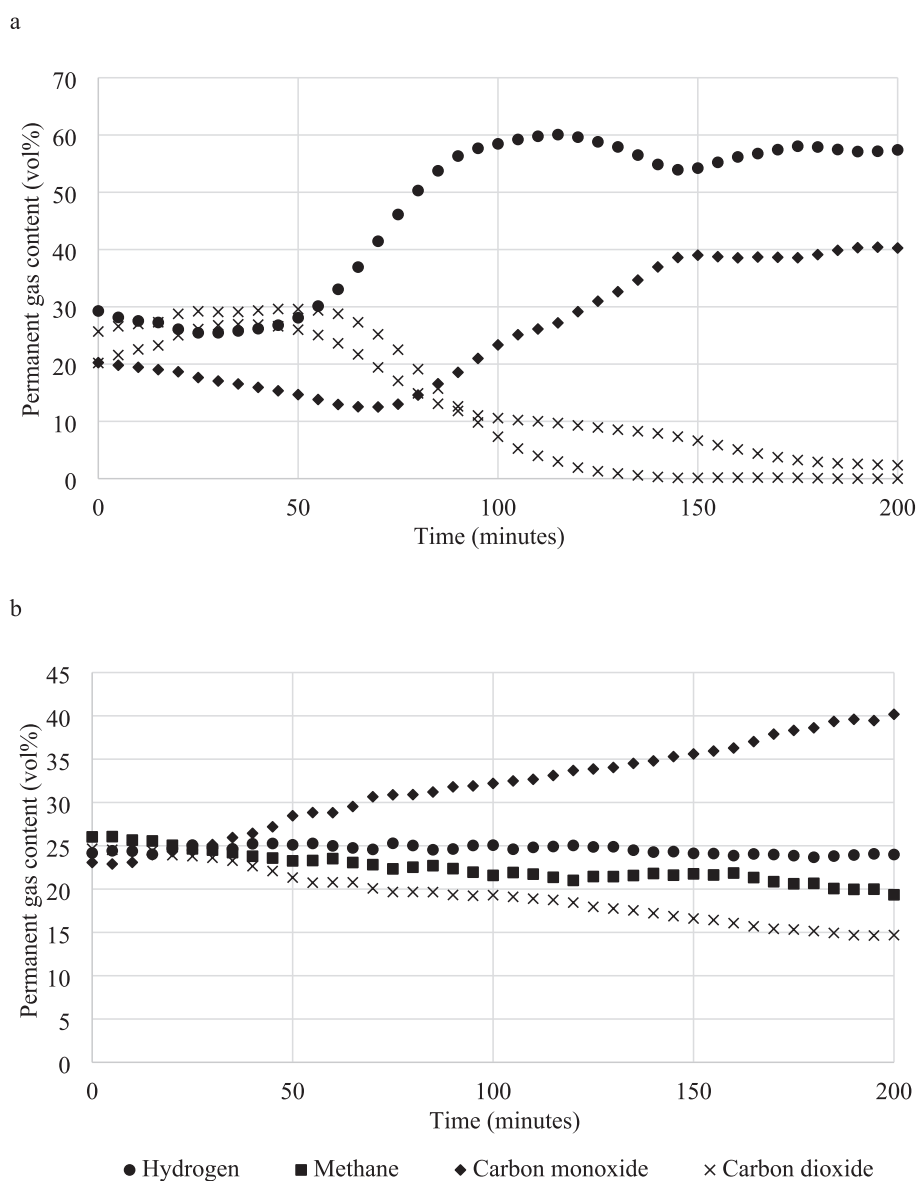
a

b

● Hydrogen   ■ Methane   ◆ Carbon monoxide   × Carbon dioxide

Fig. 3. Relative composition (volume percentage) of permanent gases derived from ensiled *Saccharina latissima* dominated macroalgal pellets produced with the Thermo-Catalytic Reforming (TCR) operated without steam reforming (TCR-dry) (plot a) and with steam reforming (TCR-steam) (plot b), throughout the experimental run. N.B. Permanent gas content (volume percentage) as a function of time for TCR-dry (a) and TCR-steam (b) methods; note data are presented on different y-axis value ranges.

concentration of hydrogen remains approximately constant (~25 vol%), the amounts of methane and carbon dioxide drop by ~10 vol%. In contrast, the proportion of carbon monoxide increases to 40 vol% after 200 min). While steam methane reforming (Eq. (3)) can account for the increasing formation of carbon monoxide, operation of this pathway alone would also result in a parallel increase in hydrogen formation, which is not observed. Instead, the less than expected proportion of hydrogen and the observed drop in carbon dioxide content is accounted for by the Water-Gas-Shift reaction (Eq. (4) [58]).

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{1}$$

$$CO_2 + C \leftrightarrow 2CO \tag{2}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{3}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{4}$$

Both TCR methods employed herein produced permanent gases with high HHV of 24.2 MJ/m^3 and 18.0 MJ/m^3 and hydrogen contents of 46.7 vol% and 24.6 vol% for TCR-dry and TCR-steam methods, respectively. The TCR-dry treatment produced higher hydrogen and HHV contents compared to the TCR-steam treatment (Table 5). In comparison to other feedstocks studied in TCR-based pyrolysis trials, the ensiled *S. latissima* dominated macroalgal pellets produce higher hydrogen contents. For example, TCR pyrolysis of waste cleansing wipes (350–450 °C) gave a hydrogen yield of 13 % (HHV of 11.0 MJ/m^3) [48]; anaerobic digestate (750 °C) produced a hydrogen yield of 35 % (HHV of 14.0 MJ/m^3) [53] and the TCR pyrolysis of wheat husks (350–450 °C) produced a HHV of 20.6 MJ/m^3 [47].

As expected, the product distribution and composition from continuous TCR pyrolysis of ensiled macroalgae is different to that achieved using static batch pyrolysis conditions. For example, Wen et al. [59] demonstrated that under batch pyrolysis beach-cast seaweed (species not identified) pyrolysed at 400, 500 and 600 °C produced lower hydrogen contents of approximately 3–24 %, depending on temperature.

A benefit of the relatively high levels of permanent gas production achieved through TCR-based pyrolysis of the ensiled *S. latissima* dominated macroalgal pellets is that these gases can be used directly as a fuel source for existing boilers, gas turbines and engines [15]. For both the TCR-dry and TCR-steam methods, reasonable hydrogen content and HHV values for the permanent gas mix were achieved, something attributed to the high mineral content of the macroalgae (35 % ash content) compared to other macroalgae [44]. The mineral content of the biomass is concentrated upon ensiling, thereby enhancing mineral-mediated catalytic cracking of the permanent gases whilst in the reformer, which in turn leads to an increase in hydrogen production [2,60]. The relatively high levels of hydrogen generation from pyrolysis of ensiled *S. latissima* dominated macroalgal pellets using the TCR-dry method suggests that this feedstock could be a promising new pathway for hydrogen-based fuel production.

Analysis of biochar from ensiled S. Latissima dominated macroalgal pellets

Analysis of the chars produced through TCR-dry and TCR-steam methods show notable differences in carbon and oxygen contents, with the char produced under steam reforming conditions having the lower carbon and oxygen contents. Under TCR-steam treatment conditions, partial oxidation of the biochar by water occurs forming carbon monoxide and then carbon dioxide, together reducing the carbon content in the biochar and hence a lower HHV, higher concentrations of sulfur and ash (Table 6) and higher product yields (mass (wt%)) (Table 3). Both TCR macroalgal processing methods produced chars with lower HHV (12.5 MJ/kg, TCR-dry and 9.6 MJ/kg, TCR-steam) compared to those of chars produced from other TCR feedstocks. For example, char from the pyrolysis of MSW had an HHV of 17.0 MJ/kg

Table 6

Relative compositional analyses of chars derived from ensiled *Saccharina latissima* dominated macroalgal pellets produced with the Thermo-Catalytic Reforming (TCR) operated without steam reforming (TCR-dry) and with steam reforming (TCR-steam).

	Char production method	
Char analyses (wt%)	TCR-dry	TCR-steam
Carbon	34.2	28.9
Hydrogen	3.0	1.3
Nitrogen	2.0	1.5
Sulfur	0.7	0.8
Oxygen (by difference)	20.4	8.2
Ash	39.8	59.3
Higher heating value (HHV) (MJ/kg)	12.5	9.6

[50], while that generated through TCR treatment of waste cleansing wipes gave a greater HHV of 30.0 MJ/kg [48]. The lower HHV of the char from ensiled macroalgae reflects the increased HHV of the permanent gas fraction. It should be noted however, that the high ash content of products from both TCR processing methods for ensiled macroalgae could be problematic if used as a source of combustion fuel at commercial scale, as the char generated would produce a high ash content requiring disposal [50].

Conclusion

Eleven out of fourteen 50 kg containers of fresh *S. latissima* dominated macroalgae successfully ensiled, preserving the biomass for a period of 30 months. Although three containers did not reach sufficient pH decrease to ensile and remain stable, likely as a result of adventitious air ingress, the methodology demonstrates the feasibility of scaling the ensiling process for macroalgae to larger-scale, commercial use. The ensiled macroalgal pellets were successfully pyrolysed, producing a large proportion of char and hydrogen-rich permanent gases with a high HHV, with the latter being of direct commercial interest. TCR treatment gave only a small fraction of bio-oil, which was accompanied by a substantial aqueous fraction. However, the bio-oil produced did have suitable properties for combustion in engines with both a high HHV and low oxygen content comparable to traditional diesel fuel. The gaseous product composition from TCR processing of the ensiled macroalgal pellets differs according to whether this is undertaken in the presence (TCR-steam) or absence of steam (TCR-dry), with a higher hydrogen content and higher HHV achieved for the permanent gases with dry reforming. Similarly, the HHV of the biochar recovered from TCR-dry process is slightly higher than that from TCR-steam reactions, as a result of partial char oxidation for the latter process. Combining ensiling of macroalgae with TCR offers a promising new pathway for the conversion of sustainably sourced marine biomass from aquaculture or biofouling by-product to energy vectors, especially to produce hydrogen.

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CRediT authorship contribution statement

Marie E. Kirby: Writing – review & editing, Writing – original draft, Visualization, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Trisha Toop: Writing – original draft, Methodology, Investigation. **Miloud Ouadi:** Writing – review & editing, Writing – original draft, Project administration, Methodology, Investigation, Formal analysis, Data curation. **Lesley McEvoy:** Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Christine Rolin:** Writing – review & editing, Resources, Project administration, Investigation. **Rhiannon Inkster:** Investigation. **Philip W. Dyer:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization, Data analysis. **Michael K. Theodorou:** Writing – review & editing, Project administration, Investigation, Funding acquisition, Conceptualization, Data analysis.

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.

Data availability

Data will be made available on request.

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