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Hydrothermal liquefaction of four brown macro-algae commonly found on the UK coasts: An energetic analysis of the process and comparison with bio-chemical conversion methods

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HIGHLIGHTS

- Bio-crudes and bio-chars were produced from hydrothermal liquefaction of four brown macro-algae.
- A new approach of studying the energy balance of the hydrothermal process was introduced.
- Reactor loading (biomass and water) and temperature have a big influence in energy balance.
- HTL of *L. saccharina* and *A. esculenta* exhibited the best energy balance.
- HTL has higher energy output than fermentation and similar with AD.

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ABSTRACT

Hydrothermal liquefaction (HTL) of four brown macro-algae was used to produce bio-crude and bio-char in an energy favorable way. Bio-crude yields between 9.8 wt% and 17.8 wt% (daf) with HHVs between 32 and 34 MJ/kg and bio-char yields between 10.9 wt% and 18.6 wt% (db) with HHVs between 15.7 and 26.2 MJ/kg were produced. A modification of the energy consumption ratio (ECR) index was attempted in order to include in the formula the calculation of the specific heat capacity of the feedstock used, as well as the increase of the specific heat capacity of water with temperature. A comparison in terms of energy output was made between the products from HTL and products from bio-chemical conversion of macro-algae such as anaerobic digestion (AD) and fermentation. The results indicate that HTL has higher energy output than fermentation and analogue of that from anaerobic digestion (7.91 $\mathrm{MJ/kg_{seaweed}}$ and 8.25 $\mathrm{MJ/kg_{seaweed}}$ from HTL and AD respectively).

1. Introduction

Recently, third generation bio-fuels have come into foreground addressing the concerns that have been raised over the effect of first and second generation bio-fuels on food prices and land use [1–3]. These ‘third generation’ bio-fuels include the utilization of wet biomass, mainly micro-algae and macro-algae. In this study the interest is in macro-algae, or seaweed, as a source of renewable fuels and chemicals. They offer a series of advantages, described elsewhere [4], compared with terrestrial biomass. Their main advantage is their relatively simple cultivation in open seas offering a vast potential area for cultivation with no competition with food crops. Thus their potential in contributing significantly to bio-energy is high.

However, the key factor is the conversion process to bio-energy. Seaweeds contain different carbohydrates than terrestrial biomass or micro-algae [5] which behave differently in the various conversion processes. Historically, conversion of seaweed into bio-energy has been examined through biochemical conversion processes such as fermentation and anaerobic digestion [6–13] while more recently thermo-chemical processes such as combustion, pyrolysis, hydrothermal liquefaction and gasification [4,5,14–23] are under investigation. From the thermo-chemical processes, hydrothermal liquefaction or hydrothermal gasification are desirable, firstly because as wet processes they are more suitable for a wet feedstock and secondly, the high alkali content of macro-algae that

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can cause problems associated with slagging and fouling during combustion and potentially during pyrolysis [7,14,15,18,22,23].

In this present study four brown macro-algae that can be commonly found in the seas of the northern hemisphere are being examined under hydrothermal conditions. More specifically four brown kelps, three belonging to the Laminariales order (*Laminaria digitata, Laminaria saccharina, Laminaria hyperborea*) and one belonging to the family of *Alariaceae* which is very closely related to Laminariales (*Alaria Esculenta*) are under investigation. The yields of the four different product streams (bio-crude, bio-char, water soluble hydrocarbons and gas) are calculated. Previous studies on hydrothermal liquefaction of macro-algae in batch reactors have shown low yields of bio-crude around 19–23 wt% [4,24] while a recent study in continuous flow reactors has shown similar bio-crude yields (8.7–27.7 wt%) [25]. The low bio-crude yields together with the high energy consumption of the hydrothermal liquefaction process (as it involves the heating of large amount of water which has very high specific heat capacity) have made necessary a comprehensive energetic analysis of the process with macro-algae as a feedstock, which is being undertaken by using two different energy ratios. Data from previous study by the authors [4] is used to examine how the different reaction conditions affect the overall energy balance of the process and these findings are applied to the present liquefaction experiments. Finally, for the first time a comparison between different conversion routes of macro-algae to energy is attempted. More specifically, the energy content of the products from HTL experiments are compared with the energy content of ethanol and methane produced by fermentation and anaerobic digestion of brown macro-algae from published data.

2. Materials and methods

2.1. Materials

Samples of *L. digitata* (LD), *L. hyperborea* (LH), *L. saccharina* (LS) and *A. esculenta* (AE) were collected from the west coast of Scotland during the summer (end of July) of 2009 by collaborative partners at the Scottish Association for Marine Sciences (SAMS). The samples were freeze dried and ground in a Retsch PM100 ball mill to a size of <90 μm before analysis. The proximate, ultimate and metal analyses of the macro-algae are listed in Table 1. The C, H, N, S content of the samples was measured using a CE Instruments Flash EA 1112 series elemental analyzer. All measurements were repeated in duplicate and a mean value is reported. The HHVs of the samples were calculated according to the equation proposed by Channiwala and Parikh [26] based on their elemental composition and ash content as described elsewhere [4]. The samples were analyzed for metals by inductively coupled plasma spectrometry (ICP) with optical emission spectroscopy (OES) on a Perkin Elmer Optima 5300DV after digestion in HNO_3 on a hot plate.

Table 1
Proximate and ultimate analysis, HHV and metal analysis of the four macro-algae.

	L. digitata	*L. hyperborea*	*L. saccharina*	*A. esculenta*
Moisture (wt%)	6.6	5.6	6.4	6.8
Ash (wt%)	23.9	16.6	21.8	25.2
C (wt%)	33.1	35.8	32.5	34.6
H (wt%)	4.7	5.1	4.5	4.7
N (wt%)	1.8	1.5	1.1	1.9
S (wt%)	0.8	0.9	0.6	0.6
O[a] (wt%)	33.9	39.1	37.9	31.1
HHV (MJ/kg)	13.1	14.2	12.2	13.9
As (ppm)	122.9	80.3	148.5	145.3
B (ppm)	76.5	45.9	68.2	108.1
Ca (ppm)	4762	2899	11185	10017
Fe (ppm)	35.5	2.9	236.2	223.0
K (ppm)	49629	42230	44427	48003
Mg (ppm)	4087	2308	3482	3592
Na (ppm)	44143	20150	26812	35032
Se (ppm)	2.7	2.9	7.3	6.8
Sr (ppm)	344	204	370	534
Zn (ppm)	21.9	5.7	7.3	20.3
Sum (ppm)	103224	67929	86743	97682

[a] Determined by difference.

2.2. Apparatus and experimental procedure

Hydrothermal liquefaction experiments were performed in a batch bomb type stainless steel reactor (75 ml, Parr, USA). The heating rate of the reactor was 25 °C min^{-1}. In a typical experiment, the reactor was charged with 8 g of seaweed biomass and 30 ml of water. The reactants were heated at 350 °C for 15 min as these conditions were found to give maximum bio-crude yield in previous study [4]. The ratio of water to biomass is based on previous calculation of the energy balance based on previous findings [4] as described in Section 3.1. After completion of the reaction, the reactor was cooled using compressed air directed towards the reactor walls.

2.3. Sample workup and analysis

Following liquefaction, the gases were vented and the reaction mixture was separated by using appropriate amounts of dichloromethane (DCM) and water. The DCM phase was separated and filtered following which the solvent was evaporated to determine the mass of the bio-crude. The bio-crude yields were expressed on (i) a dry ash free basis (daf) in order to make the comparisons with bio-crude yields from other studies (both macro and micro-algae) and (ii) on dry basis (db) in order to make the energy balance calculations according to the following Eqs. (1) and (2). The insoluble residue, making up the bio-char fraction, was weighed following air drying, and its yield was expressed on a dry basis (db) according to Eq. (3). A fraction of the aqueous phase after filtration was dried at 60 °C in a Gallenkamp Hotbox oven and the resulting products formed are described as the dissolved aqueous extracts (DAE) whose yield was calculated according to Eq. (4). The gas yield was calculated from the ideal gas law using the residual pressure and the average molecular weight of gases (30.2) found in previous [4].

$$Y_{\text{bio-crude}}(\text{daf})(\text{wt\%}) = \frac{W_{bio-crude}}{W_{seaweed} \times (100 - \text{H}_2\text{O} - Ash)} \times 100 \tag{1}$$

$$Y_{\text{bio-crude}}(\text{db})(\text{wt\%}) = \frac{W_{bio-crude}}{W_{seaweed} \times (100 - \text{H}_2\text{O})} \times 100 \tag{2}$$

$$Y_{\text{bio-char}}(\text{db})(\text{wt\%}) = \frac{W_{bio-char}}{W_{seaweed} \times (100 - \text{H}_2\text{O})} \times 100 \tag{3}$$

$$Y_{\text{DAE}}(\text{wt\%}) = \frac{W_{DAE}}{W_{seaweed} \times (100 - \text{H}_2\text{O})} \times 100, \tag{4}$$

where $Y_{\text{bio-crude}}$, $Y_{\text{bio-char}}$, Y_{DAE} are the yields of bio-crude, bio-char and dissolved aqueous extract respectively, $W_{\text{bio-crude}}$ is the mass of the bio-crude (g), W_{seaweed} is the mass of seaweed biomass fed into the reactor (g), H_2O is the water content of the seaweed, $W_{\text{bio-char}}$ is the mass of bio-char (g) and W_{DAE} is the mass of the dissolved aqueous extract (g).

The bio-crude and bio-char were analyzed for their C, H, N, S content and their HHVs were calculated with the same method described earlier in materials Section 2.1. Ash and moisture content of the bio-char as well as the boiling point distribution of