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## **Research 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.

## **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**

K. Anastasakis<sup>\*,†</sup>, A.B. Ross

*Energy and Resources Research Institute, School of Process, Environmental and Materials Engineering, University of Leeds, Leeds, LS2 9JT, UK*

## **Abstract**

Hydrothermal liquefaction (HTL) of four brown macro-algae was used to produce bio-crude and bio-char in an energy favourable way. Bio-crude yields between 9.8wt% and 17.8wt% (daf) with HHVs between 32 and 34 MJ/kg and bio-char yields between 10.9wt% and 18.6wt% (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 MJ/kg<sub>seaweed</sub> and 8.25 MJ/kg<sub>seaweed</sub> from HTL and AD respectively).

Keywords: macro-algae; liquefaction; hydrothermal; energy balance; bio-refinery; seaweed

\*<sup>†</sup> **Corresponding author:** Tel: +31 15 27 82186. E-mail: [K.Anastasakis@tudelft.nl](mailto:K.Anastasakis@tudelft.nl); [kanastasakis@gmail.com](mailto:kanastasakis@gmail.com)

**Present address:** Faculty of Mechanical, Maritime and Materials Engineering, Process and Energy Department, Energy Technology Section, Delft University of Technology, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands

## 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] and [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 can cause problems associated with slagging and fouling during combustion and potentially during pyrolysis [7], [14], [15], [18], [22] and [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 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 19-23wt% [4] and [24] while a recent study in continuous flow reactors has shown similar bio-crude yields (8.7-27.7wt%) [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 & 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 $\mu$ m 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<sub>3</sub> on a hot plate.

## 2.2. Apparatus and experimental procedure

Hydrothermal liquefaction experiments were performed in a batch bomb type stainless steel reactor (75ml, Parr, USA). The heating rate of the reactor was 25 °C min<sup>-1</sup>. In a typical experiment, the reactor was charged with 8g of seaweed biomass and 30ml of water. The reactants were heated at 350°C for 15min 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 equations (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 equation (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 equation (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].

$$Y_{\text{bio-crude(daf)}} (\text{wt}\%) = \frac{W_{\text{bio-crude}}}{W_{\text{seaweed}} \times (100 - H_2O - Ash)} \times 100 \quad (1)$$

$$Y_{\text{bio-crude(db)}} (\text{wt}\%) = \frac{W_{\text{bio-crude}}}{W_{\text{seaweed}} \times (100 - H_2O)} \times 100 \quad (2)$$

$$Y_{\text{bio-char(db)}} (\text{wt}\%) = \frac{W_{\text{bio-char}}}{W_{\text{seaweed}} \times (100 - H_2O)} \times 100 \quad (3)$$

$$Y_{\text{DAE}} (\text{wt}\%) = \frac{W_{\text{DAE}}}{W_{\text{seaweed}} \times (100 - H_2O)} \times 100 \quad (4),$$

where  $Y_{\text{bio-crude}}$ ,  $Y_{\text{bio-char}}$ ,  $Y_{\text{DAE}}$  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),  $W_{\text{seaweed}}$  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  $W_{\text{DAE}}$  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 the bio-crude were determined by thermogravimetric analysis (TGA) as described elsewhere [4]. Py-GC/MS of the DAEs was performed on a CDS 5200 series pyrolyser coupled to a Shimadzu 2010 GC-MS as described elsewhere [4].

#### 2.4. Energy Balance

In order to study the energy of the resultant products compared to the energy input of the material the energy recovery ratio (ERR) was used as proposed by Minowa et al. and Yokoyama et al. [27] and [28]. The energy recovery of starting material to oil and residue was calculated according to the following equation:

$$ERR(\%) = \frac{E_p}{E_{feed}} \times 100 = \frac{(Y_{bio-crude} \times HHV_{bio-crude}) + (Y_{bio-char} \times HHV_{bio-char})}{HHV_{feed}} \times 100 \quad (5)$$

, where  $E_p$  and  $E_{feed}$  are the energy content of the products (bio-crude and bio-char) and the starting material respectively. The product yields were expressed on dry basis (db) and high heating values on MJ/kg.

However, this relationship only describes the conversion of energy from the starting material to bio-crude and bio-char and does not take into account the energy required for the liquefaction process. Hydrothermal liquefaction is an energy intensive process as it involves heating of water which has high specific heat capacity ( $C_p$ ). In order to compare the energy content of the resultant products (bio-crude and char) with the energy required to bring the slurry of seaweed and water to the desired, temperature the energy consumption ratio (ECR) was introduced [27], [28], [29] and [30]. ECR is defined as:

$$ECR = \frac{E_l}{E_p} \quad (6),$$

, where  $E_l$  is the energy required for liquefaction (MJ/kg) and  $E_p$  is the energy of products (bio-crude and char) (MJ/kg).

When  $ECR < 1$  then the reaction is energy favourable as the products have higher energy content than that required for the reaction. When  $ECR > 1$  more energy is required for the reaction to happen than the energy content of the products.

The energy of the products ( $E_p$ ) was calculated based on their HHV and yields (on a dry basis) similar to equation (5). The energy required heating up the slurry of seaweed and water was calculated according to the following procedure: The amount of heat energy (Q) gained or lost by a substance is equal to the mass of the substance (m) multiplied by its specific heat capacity ( $c_p$ ) multiplied by the change in temperature (T):

$$Q \text{ (kJ)} = c_p \text{ (kJ/kgK)} \times m \text{ (kg)} \times dT \text{ (K)},$$

thus the energy required for the liquefaction process is:

$$E_l = Q \text{ (kJ)} = c_p \text{ (kJ/kgK)} \times m \text{ (kg)} \times dT \text{ (K)} \quad (7)$$

The specific heat capacity of a solution is given by the following equation:

$$c_{p,\text{solution}} = c_{p,\text{solids}} \times \text{wt}_{\text{solids}}\% + c_{p,\text{water}} \times \text{wt}_{\text{water}}\% \quad (8)$$

The key difference between the current proposed method and the previous methods is in calculating the specific heat capacities ( $c_p$ ) of the solids and the water. While in previous studies [27], [28], [29] and [30]  $c_p$  of solids is taken by bibliography as the  $c_p$  of wood type materials and the  $c_p$  of water is taken as constant (4.1813 J/gK), in the current study a method for calculating the  $c_p$  of every solid material is proposed and the increase in  $c_p$  of water with increasing temperature is incorporated in to the calculations.

$C_p$  of water is known and is 4.18 J/gK at 25°C. However, the  $c_p$  changes dramatically with temperature and becomes 4.51 J/gK at 200°C, 4.87 J/gK at 250°C, 5.2 J/gK at 275°C, 5.7 J/gK at 300°C, 6.82 J/gK at 325°C and 10.3 J/gK at 350°C [31]. This change in the specific heat capacity of water was implemented in the calculations for the ECR. The  $c_p$  of the solids is unknown but can be calculated by applying Kopp's rule based on their elemental composition and the heat capacities of each element:

$$C_{p,\text{solids}} = \sum x_i \times C_{p,i} \quad (9),$$

where  $x_i$  is the mass fraction of each element  $i$ , and  $C_{p,i}$  is the specific heat capacity of each element  $i$  at 25°C. Seaweed's C, H, N, S, O, K, Na, Ca and Mg content make up over 90wt% of seaweed's mass making it a very good representation for this type of biomass material. The heat capacities of these elements at 25°C are: 0.709 J/gK for C, 14.304 J/gK for H<sub>2</sub>, 1.04 J/gK for N<sub>2</sub>, 0.71 J/gK for S, 0.918 J/gK for O<sub>2</sub>, 0.757 J/gK

for K, 1.228 J/gK for Na, 0.647 J/gK for Ca and 1.023 J/gK for Mg [32]. These values increase with increasing temperature but this increase is not as significant as in water so any increase of these values with temperature was not taken into account.

According to this assumption and by applying the Kopp's rule, the specific heat capacity of any seaweed used can be calculated according to the following equation:

$$C_{p,\text{solids}} = 0.709\alpha + \frac{14.304}{2}\beta + \frac{1.04}{2}\gamma + 0.71\delta + \frac{0.918}{2}\varepsilon + 0.757\zeta, 1.228\eta + 0.647\theta + 1.023\iota \text{ (J/gK) or (kJ/kgK) (10)}$$

, where  $\alpha, \beta, \gamma, \delta, \varepsilon, \zeta, \eta, \theta$  and  $\iota$  are the mass fractions of C, H, N, S, O, K, Na, Ca and Mg of the biomass material respectively.

By substituting eq. (8) and (10) to eq. (7) and by taking account of combustion energy loss and heat recovery [28] and [29] we get:

$$E_1 = (((0.709\alpha + \frac{14.304}{2}\beta + \frac{1.04}{2}\gamma + 0.71\delta + \frac{0.918}{2}\varepsilon + 0.757\zeta, 1.228\eta + 0.647\theta + 1.023\iota) \times \text{wt}_{\text{solids}}\%) + (C_p \text{ (water)} \times \text{wt}_{\text{water}}\%)) \times m \times dT \times \frac{(1-R_h)}{R_c} \text{ (11)}$$

From this equation the heat required for the liquefaction of any mixture of water and biomass and subsequently the ECR can be calculated. Because of the significant increase in water's  $c_p$  with temperature, several temperature intervals were taken in order to solve the above equation. These intervals were: 0-200°C, 200-250°C, 250-275°C, 275-300°C, 300-325°C and 325-350°C.

### 3. Results & Discussion

#### 3.1. Energy balance

During hydrothermal liquefaction of brown macro-algae, the starting material is converted to bio-crude, bio-char, organics in water and gases. It is of interest to

evaluate the energy content of the resultant products compared to the energy content of the starting material. In order to do that the energy recovery ratio (ERR) was used (eq. 5). Only the energy content of the bio-crude and bio-char was considered in this study although it is recognised that more energy could be recovered from the water phase if a combination of technologies were considered. This ratio describes the conversion of energy from the starting material to bio-crude and bio-char. In addition, the energy consumption ratio (ECR) (eq. 6) was applied in order to study the efficiency of the hydrothermal liquefaction process. Hydrothermal liquefaction is an energy intensive process as it involves the heating of water which has a very high specific heat capacity. ECR can provide information of energy gain or loss during hydrothermal liquefaction process. Again only the energy content of the bio-crude and the bio-char was considered. When ECR is lower than 1, then the resultant bio-crude and bio-char have higher energy content than the energy needed for the reaction to occur (heating up the slurry of seaweed and water to the final temperature). When ECR is greater than 1 then there is energy loss as more energy is spent for the reaction to occur than the energy content of the products.

The two energy ratios were applied for the experimental conditions that were found to have significant influence on product yields, namely, the biomass loading and temperature [4]. The results are shown in **figure 1**. For low water loading (10 and 20 ml of water) the energy recovery is relatively high over 70%. Increasing the amount of water in the reactor leads to a gradual loss in the ERR to 55% in 30 ml of water and 50% in 40 ml of water. This is partially attributed to the reduced closure of the system with increasing water loading as it was shown previously [4]. A similar trend is observed with the ECR. Increasing the amount of water in the reactor is increasing the ECR. This was anticipated as the increase in volume of water increases

dramatically the required energy for heating due to its high specific heat capacity. Only for very low water loading (10ml) was the ECR less than 1 indicating that there is more energy content in the products than the energy consumed for the reaction. Increasing biomass loading in 30 ml of water (**figure 1, b**) was not found to have a significant influence to the ERR. For 3, 4 and 5 g in 30 ml of water the ERR was close to 60%. This was anticipated as the closure during increasing biomass loading is relatively steady (about 70%) [4]. However, increasing biomass loading has a significant effect on ECR. It was previously shown [4] that increasing biomass loading in the same volume of water does not affect the yield of the products. Thus, by increasing the biomass loading there are more available combustible products leading to the decrease of ECR. However, only biomass to water ratio 5:30 resulted in  $ECR < 1$ . The increase in temperature did not have a significant effect on the ERR resulting in typical values of 50% during all temperatures examined. Again the closure was relatively steady (about 70%) indicating that the closure of the system is proportional to the energy recovery ratio (ERR). On the other hand, increases in temperature result in an increase in ECR. The specific heat capacity of water increases significantly with increasing temperature and this is reflected to the results shown in **figure 1, c**.

The energy recovery of the system seems to be directly proportional to the closure of the system while high water loading and high temperature have negative effect in the energy balance of the system.

### 3.2. Liquefaction results

In previous study [4] it was shown that the optimum conditions (in terms of bio-crude yield) for the hydrothermal liquefaction of brown macro-algae were the

reaction of 3g of algal biomass with 30ml of water at 350°C with 15min of retention time. However, as it was shown previously by applying the ECR index that these conditions do not lead to a positive energy balance. It was shown that increasing biomass loading by keeping the same levels of water improves the overall energy balance. Furthermore, there is another advantage of increasing biomass loading as it seems to result in better bio-crude quality in terms of higher fraction of the bio-crude with low boiling point material (<250°C) [4]. By taking into account these findings, hydrothermal liquefaction of the four macro-algae under investigation were performed by reacting 8g of algal biomass with 30ml of water at 350°C with 15min of retention time.

Under these conditions the yields of the resultant products bio-crude, bio-char, DAE (dissolved aqueous extract), gases and losses are shown in **figure 2**. The bio-crude yields are expressed on a dry ash free (daf) basis while all other yields on a dry basis (db). The losses for all samples were found in similar range close to 30%. Some losses are attributed to the evaporation of light volatiles from the bio-crude during evaporation of DCM and during drying of the aqueous phase. However, these losses are not expected to be high since DCM was evaporated at room temperature while the drying of the aqueous phase took place at low temperature (60°C). This argument is supported by the high carbon recovery (~80wt%) in the three product streams (bio-crude, bio-char and aqueous phase) [4]. The majority of this mass loss is believed to be due to oxygen removal as water in the aqueous phase and possibly due to underestimation of the evolved gases with the method used. *A. esculenta* and *L. digitata* gave the highest bio-crude yields (both 13wt% on dry basis, 17.8wt% and 17.6wt% respectively on daf basis) followed by *L. saccharina* (10wt% on dry basis, 13wt% on daf basis) and *L. hyperborea* (8.1wt% on dry basis, 9.8wt% on daf basis).

Samples of *L. hyperborea* that were shown to have better fuel properties such as lower ash and metal content and higher carbon, hydrogen content and calorific value (**table 1**) were found to produce the lowest bio-crude yield. In general the samples with higher metal and ash content (*L. digitata* and *A. esculenta*) gave higher yields than the samples with lower metal and ash content. The bio-crude yield followed the K and Na content of the samples. K, Na and the bio-crudes produced from the samples follow the trend *L. digitata*>*A. esculenta*>*L. saccharina*>*L. hyperborea*. Potassium and sodium might be catalysing the reactions as their hydroxides and carbonates are catalysts commonly used during hydrothermal liquefaction of terrestrial biomass. However, seaweeds already contain high K and Na content, and as demonstrated in previous studies of catalytic HTL experiments [4], the increased KOH loading results in decreases in the bio-crude yield. This suggests that maybe a threshold in potassium or sodium concentration, above which they have negative effects on bio-crude formation. Nonetheless, this might not be the case for the lower bio-crude yields from the samples of *L. saccharina* and *L. hyperborea*. They might have higher sugar content, as shown in a previous study [4] which maybe passing in the aqueous phase during hydrothermal liquefaction.

Generally, the bio-crude yields produced from the hydrothermal liquefaction of macro-algae in the present and previous studies [4] and [24] range between 10wt% 23wt% (daf) and are substantially lower than the yields from micro-algae which typically range between 20wt% and 50wt% (daf) [29], [30] and [33]. Micro-algae have higher yields of bio-crude due to their difference in biochemical composition. They have much higher lipid content than macro-algae, most of which is easily converted to bio-crude under hydrothermal conditions, while the carbohydrates, which are the dominant fraction of macro-algae are converted at a lesser extent [29].

**Table 2** lists the ultimate analysis and the HHVs of the produced bio-crudes. All bio-crudes were found to have similar elementary content resulting in similar HHVs (32-34 MJ/kg). However, their oxygen content was higher than the bio-crudes produced at lower biomass loading resulting in lower HHV [4]. Nonetheless, the material with boiling range <250°C present in the bio-crudes has increased significantly compared to those of lower biomass loading as shown in previous studies [4]. The bio-crude fraction with boiling range <250°C ranges between 35wt% and 40wt% for all the samples (**table 3**) and is comparable with the typical crude oil's fraction (44.2wt%) [34]. However, the bio-crudes were found to contain significant amount of nitrogen (3-4wt%) and sulfur (0.6-0.8wt%). These compounds will result in NO<sub>x</sub> and SO<sub>x</sub> emissions upon combustion of the bio-crude are a serious challenge for hydrothermal liquefaction of high nitrogen feedstocks. Similar problems have been raised with the bio-crude from hydrothermal liquefaction of micro-algae where the N content of the bio-crude is much higher (5-9wt%) [29], [30] and [33]. This is largely attributed to the higher protein content of micro-algae suggesting that the nitrogen in the bio-crude results from the protein content of the feedstock. A solution to this problem could be the extraction of proteins prior to conversion but as Biller and Ross [29] demonstrate, a significant amount of protein (20wt%) is converted into bio-crude, so for a feedstock such as macro-algae with low lipid content and low bio-crude yields extraction of proteins is undesirable. The other solution is upgrading of the biocrude by denitrogenation and desulfurization following hydrothermal liquefaction.

The bio-char yields follow the trend *L. saccharina*>*A. esculenta*> *L. hyperborea*> *L. digitata* (18.6wt%, 17.9wt%, 16.7wt% and 10.9wt% respectively). *L. digitata* was found to produce a relatively high bio-crude yield but the bio-char yield

was the lowest out of all samples. The rest of the samples had similar bio-char yields with *A. esculenta* having high yields in both bio-crude and bio-char. **Table 4** lists the proximate and ultimate analysis as well as the HHVs of the bio-chars produced.

Unlike the case of bio-crudes which all have similar fuel properties, the bio-chars were found to significantly differ in their properties. Bio-char produced from *L. hyperborea* have the best fuel properties with high carbon and low ash contents resulting in a relatively high HHV (26.2 MJ/kg). On the other hand, char produced from *L. digitata* (15.7 MJ/kg) had the lowest HHV while chars produced from *L. saccharina* and *A. esculenta* had similar properties and HHV (17.2 and 18.3 MJ/kg respectively).

*A. esculenta* was found to produce both bio-crude and bio-char in high yields and with high calorific value, indicating the better performance of this feedstock under hydrothermal conditions. This is evident by the better energy balance of this specific sample as indicated in **table 5**. This table lists the yields of bio-crudes and bio-chars on a dry basis (db) together with their heating values (HHV) and the calculated energy recovery ratios (ERR) and energy consumption ratios (ECR). *A. esculenta* was found to have the highest ERR (63.84%) indicating that the majority of energy content of the starting feedstock has passed in to the bio-crude and bio-char fraction during hydrothermal liquefaction. *L. hyperborea* was the sample with the next highest ERR mostly because of the very high HHV of its bio-char, followed by *L. saccharina* and *L. digitata*. *L. digitata* in spite of having relatively high, bio-crude yield, has the lowest energy recovery (less than 50%) because of its very low bio-char yield. The energy consumption ratio (ECR) followed the same trend, being better (lower) for *A. esculenta*, followed by *L. hyperborea*, *L. saccharina* and *L. digitata*. ECR was found lower than 1 for all samples indicating that there is the possibility of

net energy production under the given conditions in the given system. However, the energy balance was calculated according to the setup of the specific batch reactor. If hydrothermal liquefaction of macro-algae is to be used for mass production of bio-crude and bio-char, a continuous rather than a batch system might be preferable and the energy balance is likely to be better. Such a continuous system is described in a recent work by Elliott and co-workers [25]. Also the heating value of the gases and the energy content of the aqueous phase have to be taken into account. As it was previously shown [4] the gases contain hydrogen and methane, two gases with high heating values that can contribute significantly in the overall energy balance, while a significant amount of sugars is present in the aqueous phase. However, this investigation was concentrated into the heavy organic products from hydrothermal liquefaction rather than the gaseous and the dissolved in water products.

The organics dissolved in water follow the trend *L. hyperborea* > *L. digitata* > *A. esculenta* > *L. saccharina* (36.1wt%, 35.4wt%, 30.4wt% and 28.5wt% respectively). A fraction of the aqueous phase was dried and the resultant dried aqueous extracts were pyrolyzed in order to identify the origin of the compounds dissolved in water. **Figure 3** illustrates the main volatiles evolved during pyrolysis of the dried aqueous extracts. The graph compares the corrected peak intensities based on uniform mass. The results are in agreement with previous study [4] where cyclopentenones, dianhydromannitol and acetylfuran were the main volatiles evolved during pyrolysis of DAEs from HTL at 350°C. The presence of sugar (mannitol and laminarin) originated volatiles such as dianhydromannitol, acetylfuran and isosorbide [5] are confirming the presence of sugars in the aqueous phase, indicating the possibility of further utilization of the aqueous phase from HTL of macro-algae.

### 3.3. Comparison of liquefaction products with biochemical conversion methods products in terms of energy output

Hydrothermal liquefaction has been successfully demonstrated as a process for producing liquid (bio-crude) or solid (bio-char) fuels from brown macro-algae.

Hydrothermal liquefaction is considered one of the most suitable thermochemical processes for converting macro-algae into energy because of its ability to handle wet feedstock and remove the alkali metals from the combustible products. Combustion and pyrolysis on the other hand, require dry feedstock. Furthermore, combustion of brown macro-algae has been shown not to be preferable because of the problems the high alkali content of seaweed is going to create in the combustion chambers [14], [15], [16], [18], [21] and [22]. Pyrolysis reactors might experience the same problems due to the high alkali content.

However, there are other alternative processes for producing energy from seaweed, through biochemical conversion routes. These conversion methods, fermentation to ethanol and anaerobic digestion to methane, also utilise wet feedstock such as macro-algae. It was of interest to compare how these biochemical processes compare with hydrothermal liquefaction on energy content of product yields. In order to do that, data from published work for fermentation of brown macro-algae [6], [7], [11] and [12] as well as data from published work for anaerobic digestion of brown macro-algae [7], [8], [9], [10] and [13] were compared with the results of this study. By taking into account the HHVs and densities of ethanol and methane as well as the yields of the products, the energy output of ethanol and methane from 1kg of dry macro-algae could be compared with the energy output with the two liquefaction products (bio-crude and bio-char).

Horn et al. [12] used autumn harvested fronds of *L. hyperborea* to extract mannitol and laminarin and subsequent fermentation of these extracts to produce ethanol. They used 1kg (wet weight) of *L. hyperborea* which yielded 20g/l extract (mannitol and laminarin). The best ethanol yield was found to be  $0.43 \text{g}_{\text{ethanol}}/\text{g}_{\text{extract}}$  during a batch culture. Assuming a maximum dry weight of 10% of *L. hyperborea* this means that 100g of dry seaweed produces 20g of mannitol and ethanol extract which produces a total of  $8.6 \text{g}_{\text{ethanol}}$ . Thus the ethanol yield was 8.6wt%. Ethanol has a HHV of 29.7MJ/kg so 1kg of seaweed on a dry weight would give 2.554MJ of energy. The authors found that mannitol was the preferred substrate in batch fermentations while in continuous fermentations laminarin was the preferred one.

In another study by the same authors [11] they used synthetic mannitol for fermentation to yield a maximum of  $0.38 \text{g}_{\text{ethanol}}/\text{g}_{\text{mannitol}}$ . According to Black [35] mannitol can reach a maximum content of 30% in seaweed. By assuming this maximum mannitol content the yield becomes  $0.114 \text{g}_{\text{ethanol}}/\text{g}_{\text{seaweed}}$  (11.4wt%). At this maximum yield and by taking account the HHV of ethanol, 1kg of seaweed on a dry weight would give 3.386MJ of energy if all the mannitol present in the sample could be utilised.

Adams et al. [6] found a quite low ethanol yield from the fermentation of the brown macro-alga *L. saccharina*. Of course the fermentations in this study were not optimised and the mannitol component was not used. They found maximum ethanol yields of 0.45% v/v. By taking into account the procedure of preparing the substrates and the density of ethanol this translates into  $0.014202 \text{g}_{\text{ethanol}}/\text{g}_{\text{seaweed}}$  (1.42wt%). By taking into account the density of ethanol ( $0.789 \text{kg}/\text{m}^3$ ) and its HHV (29.7 MJ/kg), 1 kg of dry seaweed would produce 0.42 MJ of energy ( $0.42 \text{MJ}/\text{kg}_{\text{seaweed}}$ ).

On a later study Adams et al. [7] found that July harvested samples of *L. digitata* would produce the highest yield of ethanol ( $167 \mu\text{l}_{\text{ethanol}}/\text{g}_{\text{seaweed}}$ ). Following the same procedure (with density and HHV of ethanol), 1 kg of dry seaweed would produce 3.9 MJ of energy ( $3.9\text{MJ}/\text{kg}_{\text{seaweed}}$ ).

The other possibility for energy generation from brown macro-algae through biochemical processes is by anaerobic digestion. Hanssen et al. [10] investigated the biogas production from three brown macro-algae (*L. hyperborea*, *L. saccharina* and *A. nodosum*) and found maximum methane yield of  $0.28 \text{ l}_{\text{CH}_4}/\text{g}_{\text{VS}}$  during semicontinuous cultures of *L. hyperborea*. The yield was expressed in volatile solids (VS), the percentage of which in the sample used was unusually high for brown seaweed (77.5%). By taking into account this volatile solid content methane yield becomes  $0.217 \text{ l}_{\text{CH}_4}/\text{g}_{\text{seaweed}}$ . By taking into account the density ( $0.68\text{kg}/\text{m}^3$ ) and the HHV of methane ( $55.5\text{MJ}/\text{kg}$ ), if 1kg of dry seaweed was to be used the energy output of the resultant methane would be 8.189MJ ( $8.19 \text{ MJ}/\text{kg}_{\text{seaweed}}$ ).

Similar results were found by Adams et al. [7] where 219 ml of methane per gram of seaweed ( $0.22 \text{ l}_{\text{CH}_4}/\text{g}_{\text{seaweed}}$ ) were produced during anaerobic digestion of July harvested samples of *L. digitata*. Following the same procedure (density and HHV of  $\text{CH}_4$ ), this translates of 8.25 MJ of energy per kg of dry seaweed digested ( $8.25 \text{ MJ}/\text{kg}_{\text{seaweed}}$ ).

Other studies on anaerobic digestion have shown lower methane yields. Fernandez et al. [8] produced 4.42 MJ and 4.41 MJ of energy per kg of dry seaweed ( $0.1173 \text{ l}_{\text{CH}_4}/\text{g}_{\text{seaweed}}$  and  $0.1171 \text{ l}_{\text{CH}_4}/\text{g}_{\text{seaweed}}$  respectively) by digesting two brown algae *Macrosystis pyrifera* and *Durvillea antarctica* respectively. Similarly, Troiano et al. [13] produced 4.96 MJ and 4.56 MJ of energy per kg of dry seaweed ( $0.1315 \text{ l}_{\text{CH}_4}/\text{g}_{\text{seaweed}}$  and  $0.121 \text{ l}_{\text{CH}_4}/\text{g}_{\text{seaweed}}$  respectively) by digesting *Laminaria saccharina* at

two different feeding ratios. Gurung et al. [9] found slightly higher methane yield during anaerobic digestion of a brown algae (not mentioning the specie). They produced 6.14 MJ of energy per kg of dry seaweed.

In order to make a comparison between biochemical conversion processes and thermochemical conversion via hydrothermal liquefaction, the previous liquefaction yields (on a dry basis) of the combustible products (bio-crude and bio-char) were expressed in terms of their energy output (MJ/kg<sub>seaweed</sub>). The formula used was:

$$E_{\text{output}} = (\text{wt}\%_{\text{bio-crude(d.b.)}} \times \text{HHV}_{\text{bio-crude}}) + (\text{wt}\%_{\text{bio-char(d.b.)}} \times \text{HHV}_{\text{bio-char}})$$

Thus, by assuming the liquefaction of 1kg of dry seaweed, the bio-crude and bio-char from *Laminaria digitata*, *Laminaria hyperborea*, *Laminaria saccharina* and *Alaria esculent* produce 5.89 MJ/kg<sub>seaweed</sub>, 7.05 MJ/kg<sub>seaweed</sub>, 7.91 MJ/kg<sub>seaweed</sub> and 7.67 MJ/kg<sub>seaweed</sub> respectively.

Summarizing, fermentation of brown macro-algae was found to have the lowest energy output (2.55-3.9 MJ per kg seaweed fermented), while anaerobic digestion and hydrothermal liquefaction have similar energy output (4.41-8.25 MJ and 5.89-7.91 MJ per kg seaweed digested and liquefied respectively). The lower energy output through fermentation was expected as fermentation utilizes only the sugar fraction (mannitol and laminarin) present in macro-algae while the other two processes utilize more algal components. According to Gunaseelam [36] mannitol and alginates are the most biodegradable carbohydrates during anaerobic digestion while no studies on the liquefaction ability of the different carbohydrates (alginates, mannitol, laminarin and fucoidan) of brown macro-algae have been conducted.

Anaerobic digestion has a slightly higher energy output than hydrothermal liquefaction. However, hydrothermal liquefaction is not yet as well established process as AD and as was shown in previous studies [4] the gases produced, contain

CH<sub>4</sub> and H<sub>2</sub> which once taken into account would increase its energy output.

Furthermore in the same study (also in the present one) was shown that a large fraction of the sugars present (mannitol and laminarin) in macro-algae are passing in the liquefaction water phase which could be potentially used as a feedstock for further fermentation of the sugars to ethanol. Similarly it would be of interest to examine the potential of producing bio-crude and bio-char from the digestate of anaerobic digestion (as it contains significant amount of carbon) in order to combine the two processes for increasing the energy output, in a bio-refinery concept.

Hydrothermal liquefaction (HTL) and anaerobic digestion (AD) seem to be the two competing processes for energy generation from macro-algae. AD has slightly higher energy output and is a less energy intensive process. On the other hand HTL has the ability to increase its energy output by utilizing the produced gases and the dissolved sugars, but is also a more energy intensive process. Different design of the HTL system (e.g. continuous HTL or use of concentrated solar power to heat up the reactor) could reduce or eliminate the energy needs of the process. Another crucial factor when comparing the two processes is the chemicals and other additives that are used in each process. HTL of macro-algae is achieved just by heating the sample with water, while in AD frequently the samples have to be washed, glucose is used as a feed in the reactors and a nutrient media containing a variety of chemicals has to be used. Finally, the two routes produce different products and must be taken into account when considering the two processes. AD produces a gaseous fuel (CH<sub>4</sub>) while HTL produces primarily a liquid (bio-crude) and solid fuel (bio-char).

#### **4. Conclusions**

HTL conversion of four brown macro-algae produced bio-crudes with similar heating values, however the bio-chars produced had a bigger variation in their HHVs. Both products were found high in N content indicating the necessity of upgrading before being used as fuels. The effect of biomass loading and temperature on the energy balance of the process was shown. HTL was shown to produce bio-crude and bio-char with an energy favorable way. The modified energy calculations allow a more accurate description of the energy consumption during batch experiments. A comparison of the energy yields per Kg of biomass indicate that hydrothermal liquefaction compares similarly to AD, both of which are higher than fermentation.

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**Table 1** Proximate and ultimate analysis, HHV and metal analysis of the four macroalgae.

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

<sup>a</sup> determined by difference

**Table 2** Ultimate analysis, HHVs and yields of the bio-crudes produced from hydrothermal liquefaction of the four macro-algae samples.

	<i>L. digitata</i>	<i>L. hyperborea</i>	<i>L. saccharina</i>	<i>A. esculenta</i>
<b>Yield (wt%) (daf)</b>	17.6	9.8	13	17.8
<b>C (wt%)</b>	70.5	72.8	74.5	73.8
<b>H (wt%)</b>	7.8	7.7	7.9	8
<b>N (wt%)</b>	4.0	3.7	3.0	3.8
<b>S (wt%)</b>	0.7	0.82	0.6	0.8
<b>O* (wt%)</b>	17	14.9	14.0	14.0
<b>HHV (MJ/kg)</b>	32	33	33.9	33.8
<b>H/C</b>	1.32	1.27	1.28	1.3
<b>O/C</b>	0.18	0.15	0.14	0.14

\*determined by difference

**Table 3** Boiling point distribution of bio-crudes obtained from hydrothermal liquefaction of the four macro-algae samples (determined by TGA).

	<i>L. digitata</i>	<i>L. hyperborea</i>	<i>L. saccharina</i>	<i>A. esculenta</i>
<b>40-200°C</b>	24.64	23.01	19.13	20.78
<b>200-250°C</b>	13.09	16.89	15.78	14.20
<b>250-300°C</b>	13.21	14.96	14.10	14.10
<b>300-350°C</b>	11.29	11.70	11.78	11.83
<b>350-400°C</b>	11.72	9.43	12.78	12.14
<b>400-450°C</b>	5.62	1.62	5.26	5.15
<b>450-500°C</b>	1.03	1.37	0.82	1.35
<b>500-550°C</b>	1.10	3.46	1.17	1.29
<b>&gt;550°C</b>	3.80	4.54	3.86	3.29

**Table 4** Proximate and ultimate analysis, HHVs and yields of the bio-chars produced from hydrothermal liquefaction of the four macro-algae samples.

	<i>L. digitata</i>	<i>L. hyperborea</i>	<i>L. saccharina</i>	<i>A. esculenta</i>
<b>Yield (wt%) (db)</b>	10.9	16.7	18.6	17.9
<b>Moisture<sup>a</sup> (wt%)</b>	3.3	1.9	3.1	3.6
<b>Ash<sup>a</sup> (wt%)</b>	38.6	14.5	33.8	35.1
<b>C (wt%)</b>	39.1	64.2	44.2	45.3
<b>H (wt%)</b>	3.1	4.3	3.1	3.3
<b>N (wt%)</b>	2.2	3.0	1.8	2.3
<b>S (wt%)</b>	2.1	0.6	0.3	0.8
<b>O<sup>b</sup> (wt%)</b>	8.4	9.5	10.7	6.0
<b>HHV (MJ/kg)</b>	15.7	26.2	17.2	18.3
<b>H/C (daf)</b>	0.94	0.80	0.84	0.87
<b>O/C (daf)</b>	0.16	0.11	0.18	0.10

<sup>a</sup> determined by TGA

<sup>b</sup> determined by difference

**Table 5** Energy balance for hydrothermal liquefaction products of the four macro-algae samples.

	<i>L. digitata</i>	<i>L. hyperborea</i>	<i>L. saccharina</i>	<i>A. esculenta</i>
<b>Bio-crude yield (wt%) (db)</b>	13	8.1	10	13
<b>Bio-crude HHV (MJ/kg)</b>	32	33	33.9	33.8
<b>Bio-char yield (wt%) (db)</b>	10.9	16.7	18.6	17.9
<b>Bio-char HHV (MJ/kg)</b>	15.7	26.2	17.2	18.3
<b>ERR</b>	49.08	58.6	54.77	63.84
<b>ECR</b>	0.78	0.65	0.69	0.6

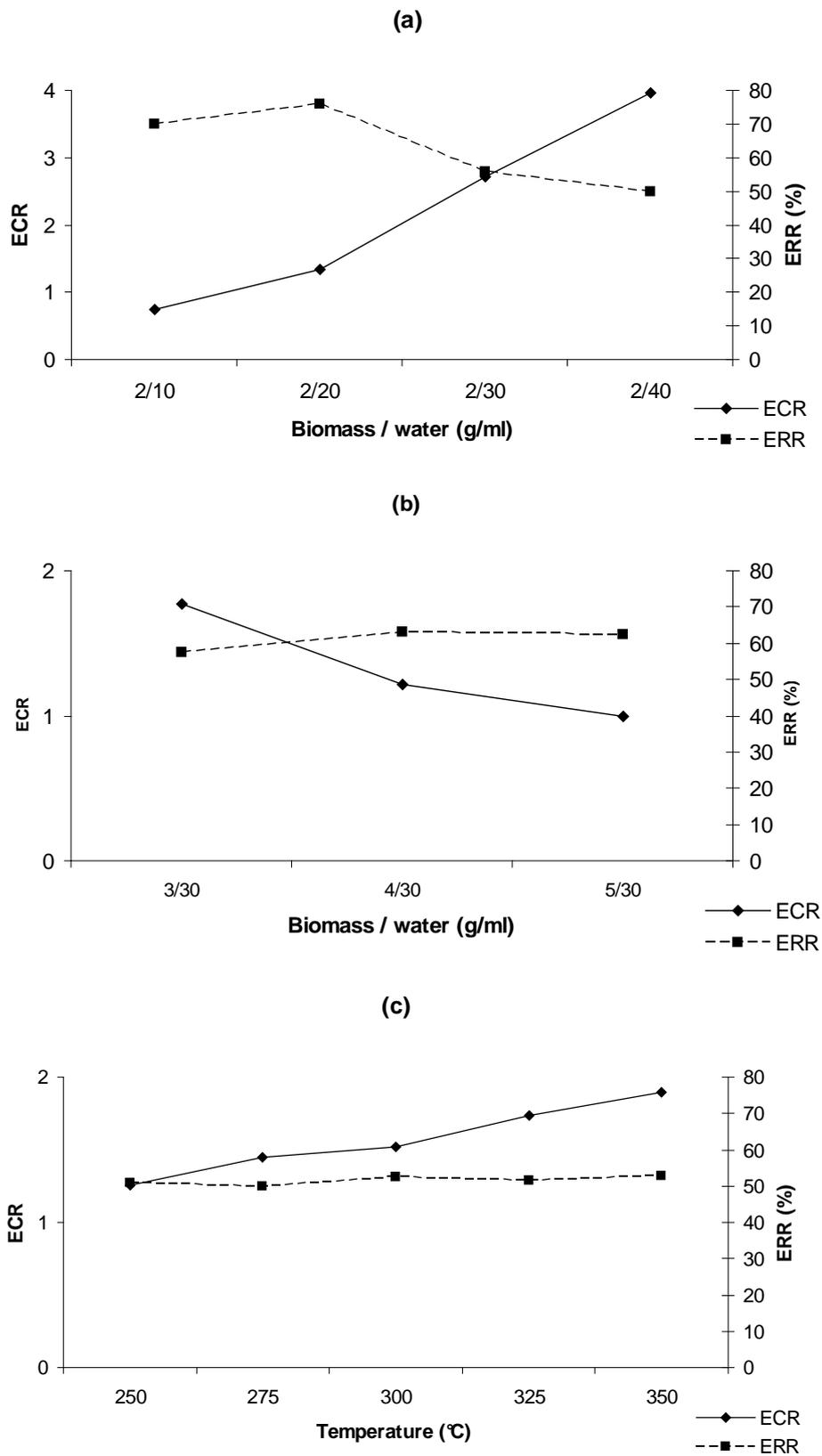
## Figure captions

**Figure 1** Energy Conversion Ratio (ECR) and Energy Recovery Ratio (ERR) as a function of (a) water loading, (b) biomass loading and (c) temperature.

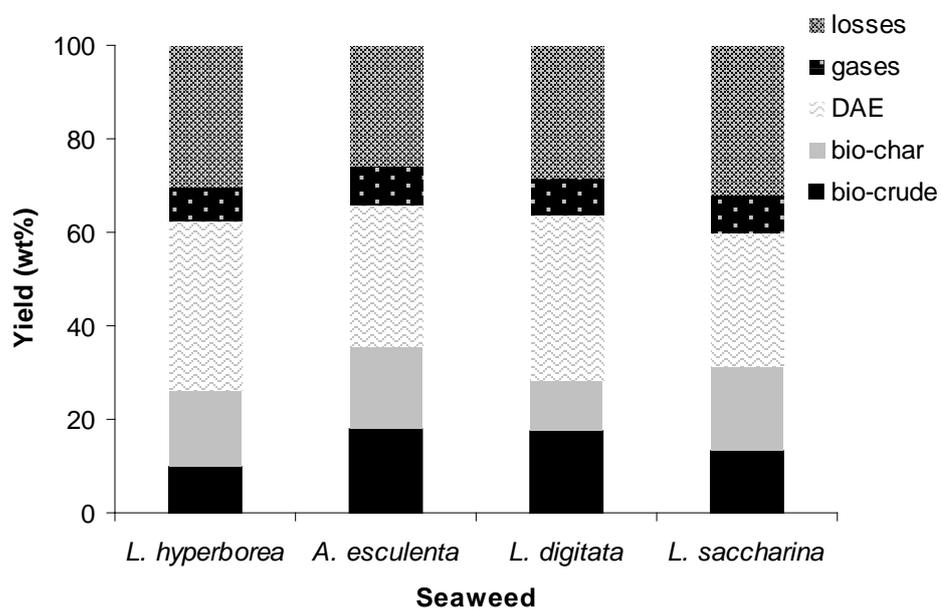
**Figure 2** Yields of products from hydrothermal liquefaction of *L. hyperborea*, *A. esculenta*, *L. digitata* and *L. saccharina*.

**Figure 3** Main volatiles evolved during py-GC/MS of the dried aqueous extracts.

Figure 1



**Figure 2**



**Figure 3**

