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Suitability of hydrothermal liquefaction as a conversion route to produce biofuels from macroalgae

Diego López Barreiro [a,*], Mario Beck [b], Ursel Hornung [b], Frederik Ronsse [a], Andrea Kruse [b,c], Wolter Prins [a]

[a] Department of Biosystems Engineering, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium
[b] Institute for Catalysis Research and Technology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmoltz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
[c] Conversion Technology and Life Cycle Assessment of Renewable Resources (440f), Institute of Agricultural Engineering, University Hohenheim, Garbenstrasse 9, 70599 Stuttgart, Germany

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ABSTRACT

The brown algae *Fucus vesiculosus*, *Laminaria saccharina* and *Alaria esculenta* were subjected to hydrothermal liquefaction (HTL) for 15 min at 350 °C in batch microautoclaves. Further optimization was carried out in view of optimizing the biocrude oil yield, varying the temperature from 330 to 370 °C. The maximum conversion to biocrude was 29.4 ± 1.1 wt.% at 360 °C for *A. esculenta*. The reaction pathways for macroalgae HTL and its capability for recycling nutrients were also investigated. The aqueous phase showed potential for a partial recovery of the nitrogen (21.2–28.6 wt.%) and sulfur (25.8–34.6 wt.%) from the initial biomass, and an almost total recovery of potassium and sodium. Results indicate that HTL as a sole conversion method to produce biofuel as single product is not recommended for macroalgae due to the low conversion to biocrude oil. At such conditions, its use as post-treatment for the remaining biomass after extracting valuable compounds (especially from the carbohydrate fraction) might be more interesting, and is suggested as the future direction for research.

1. Introduction

In recent years, much interest and research efforts have been placed in aquatic biomass as source of third generation biofuels. Their advantages over other types of biomass have been widely reviewed, as well as their disadvantages [1,2]. Most of the attention has been devoted to microalgae. However, one of the main economic hurdles associated with the conversion of microalgae to biofuels is the energy cost of harvesting them [3]. The harvest is a required step to obtain a concentration high enough to enable a further processing via conversion techniques such as hydrothermal liquefaction (HTL), a process that allows obtaining a liquid biofuel using hot compressed water (10–25 MPa, 300–375 °C). Such a technique is therefore especially suited for wet biomass.

The energy costs of harvesting are not so troublesome when considering macroalgae (also known as seaweeds) due to their larger size. Macroalgae differ from lignocellulosic and microalgal biomass in many aspects [4], like the biochemical composition: they have carbohydrates different from lignocellulosic biomass (i.e., laminarin, mannitol) and proteins as main compounds, and they do not present a significant content of lipids (as microalgae do). Another remarkable aspect is the seasonal variability of their biochemical composition, extremely large in comparison to the more stable lignocellulosic biomass. It is highly influenced by the solar radiation, the temperature and the availability of nutrients, among other factors.

Macroalgae are a very interesting biomass source. They are not a typical food source (with some exceptions like Japan) and they do not compete with any other land use, being the biomass with the highest growth rate at high latitudes [5]. The FAO reported that the annual production of seaweeds increased in the last decade on average more than 7.5% yearly [6], showing the growing interest in this biomass type. In terms of carbon capture from the atmosphere, Chung et al. [7] indicated that macroalgae provide a way of removing around 1 Pg of carbon per year at the current production rates.

Macroalgae are a renewable source for many interesting products, and have a wide range of applications. They can be used to produce alginates, fodder, chemicals, health or body care products [2,8]. All these products have market values higher than biofuels, but their recovery leaves behind waste biomass that needs to be processed to minimize the production of residues. In this sense, the typical routes used for producing energy from macroalgae are biogas production via anaerobic digestion and fermentation for bioethanol production [2].

In this work, we explore the possibility of obtaining biofuels from brown seaweeds via hydrothermal processing. To the present, some studies have already investigated the hydrothermal conversion of macroalgae to biocrude oil. Zhou et al. [9] liquefied *Enteromorpha prolifera* at temperatures ranging from 220 to 320 °C, attaining a maximum biocrude oil yield of 23.0 wt.% (dry basis). A higher yield was reported by Li et al. [10] via HTL of *Sargassum patens* C. Agardh, achieving a conversion of 32.1 wt.% (dry, ash free; daf) at 15 min of

* Corresponding author.
E-mail address: Diego.LopezBarreiro@UGent.be (D. López Barreiro).

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reaction time and 340 °C. Anastasakis and Ross [11] liquefied the brown algae *L. saccharina* and obtained a maximum oil yield of 19.3 wt.% (daf) at 350 °C and 15 min. Schumacher et al. [12] investigated the hydrothermal gasification of four species (*Fucus serratus*, *Laminaria digitata*, *A. esculenta* and *Bifurcaria bifurcata*), reporting the production of a gas rich in hydrogen and methane, and suggesting that the salts present in macroalgae were enhancing the production of gas under hydrothermal conditions. Li et al. [13] converted *Laminaria japonica* to biocrude oil over a modified zeolite, achieving a maximum conversion to biofuel of 15.32 wt.% (dry basis). Neveux et al. [14] converted six species of macroalgae from marine and freshwater environments. The species leading to the highest conversion to biocrude oil was *Oedogonium* (35.9 wt.%, daf). Bach et al. [15] studied the effect on HTL of *L. saccharina* of the heating rate at which the reaction temperature was achieved (from 136 to 585 °C·min^{-1}). They reported that increasing the heating rate had a beneficial effect on the biocrude yield, achieving a maximal conversion of 79 wt.% (daf) at 350 °C, 15 min and a heating rate of 585 °C·min^{-1}. The surprisingly high yield was attributed to the effect of high heating rates that would reduce undesired side-reactions to other product phases and promote the formation of biocrude as main product. Although this effect might be true, it was recently proved that the results from Bach et al. [15] cannot be correct, showing some inconsistencies in the energy and mass balances [16]. Very recently, Anastasakis and Ross [17] converted four types of brown algae (*L. digitata*, *L. saccharina*, *Laminaria hyperborea* and *A. esculenta*), obtaining biocrude oil yields ranging from 10.9 to 18.6 wt.% (dry basis). The only attempt to liquefy macroalgae in a continuous set-up was reported by Elliott et al. [18], converting *Saccharina* spp. into biocrude oil and obtaining a maximum yield of 27.1 wt.% (daf basis). They reported that most of the organic matter remained in the aqueous product.

In this study the species *A. esculenta*, *F. vesiculosus* and *L. saccharina*, all of them belonging to the class Phaeophyceae (brown), were subjected to HTL. The aim of these experiments was to study the variation in the suitability for HTL of species belonging to the same class. The fate of mineral matter (present in high amounts in marine waters) throughout the process was also investigated, in view of providing ways to recover nutrients through this process. Finally, the molecular composition of the aqueous and oily products was analyzed in detail by means of several techniques to provide a scheme of the reaction pathways for HTL of seaweeds.

2. Materials and methods

2.1. Macroalgae strains

A. esculenta was supplied in a dry form by the company Dingle Bay Seaweed (Ireland), and *F. vesiculosus* and *L. saccharina* were collected on the coast from the region of Bretagne (France). The dry weight was determined by drying the algae overnight at 105 °C, and the ash content by treating them at 550 °C for 5 h in the presence of air. To characterize the organic content of the algae, a modified version of the method proposed by Zhu and Lee [19] was used. The determination of the organic content of macroalgae can be overestimated by the presence of inorganic salts dissolved in water that accumulate with the algae during harvesting and drying. Therefore, these salts need to be removed before determining the organic content of the macroalgal feedstock. For this reason, around 0.3 g of dry feedstock was washed in a filter (S&S 589[3] blue ribbon) with distilled water (300 mL) to remove inorganic salts from the surface of the algae. Thereafter, the algae were dried overnight in an oven at 105 °C. The variation of weight was assumed to be caused by the loss of salts entrained during the washing step. The dry algae matter was then ashed at 550 °C for 5 h in the presence of air. The variation between the dry weight after washing away the salts and its ash content represented the organic mass of the seaweeds. For further discussion about this topic, the reader is referred to Zhu and Lee [19].

The elemental composition (CHNS) of the feedstock was measured (in wt.%) by a Vario EL III device (oxygen was measured by difference), and the content of inorganic matter was investigated by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a 720/725-ES emission spectrometer with a CCD detector from Agilent Technologies. The elemental composition was used in Boie's formula (Eq. (**1**)) [20] to calculate the Higher Heating Value (HHV).

$$HHV_{Boie}\,(MJ\cdot kg^{-1}) = 0.3516\cdot C + 1.16225\cdot H - 0.1109\cdot O + 0.0628\cdot N \quad (1)$$

The protein, fiber and lipid contents were analyzed at the LA Chemie department (University of Hohenheim), following the standard procedures from the EC Regulation 152/2009.

2.2. Hydrothermal liquefaction (HTL)

The macroalgae were liquefied in microautoclaves with a volume of 10 mL made of stainless steel EN 1.4571. Each microautoclave consists of an inner cylindrical container with a metal-on-metal seal with a metal lid, inserted into two hollow cylindrical elements that are screwed together. The microautoclaves can withstand pressures of up to 40 MPa and a maximum temperature of 673 K. 70% of the volume of the inner cylindrical container was filled with an algae–water mixture (weight ratio of 1:10). The headspace was purged with nitrogen to remove the residual air present in the free volume, and then 2 MPa of N_2 were loaded to the microautoclave before closing it with a torque key.

The microautoclaves were then introduced in a GC-oven that allowed controlling the reaction temperature. A heating rate of approximately 18 °C·min^{-1} was used to achieve the reaction temperature (350 °C), resulting in a heating time of 18.4 min. Once this temperature was attained inside the microautoclave, it was maintained for 15 min. After finishing the holding time, the microautoclaves were inserted in an ice bath for quenching. For *A. esculenta*, additional experiments were done at different temperatures (from 330 to 370 °C) to study the biocrude oil yield as a function of temperature. The heating times applied varied between 17.2 and 19.7 min. All the experiments were done at least in triplicate, and the results show their average and standard deviation values. The product yields were subjected to a one-way analysis of variance (ANOVA) at a significance level of $\alpha = 0.05$ to assess the effect of varying the type of strain and the temperature.

2.3. Product separation and analysis

The yield of the different product phases was calculated on an organic basis as the ratio of the weight of the recovered organic mass (m_i) and the mass of microalgae (daf) initially loaded to the reactor, according to Eq. (2):

$$Yield(wt\%) = \frac{m_i}{m_{micoalgae(daf)}}100. \quad (2)$$

Firstly, the microautoclaves were opened in a sealed container of a known volume connected to a pipe that had a manometer and that was closed at the opposite end by a valve (Fig. 1). The system was previously purged with nitrogen to remove any air that could be present in it. After opening the microautoclave, the pressure in the container was recorded and a gas sample was taken from a sampling container with a septum for analysis with a gas chromatograph. By means of the ideal gas law, the amount of gas was calculated, using the pressure recorded, the volume of the sealed container and the composition measured with the gas chromatograph. The calculated mass was used in Eq. (2) to obtain the gas yield.

The composition of the gas was measured by injecting manually 100 μL of the gas sample in an Agilent 7890A gas chromatograph with