



Full Length Article

Valorization of *Sargassum tenerrimum*: Value addition using hydrothermal liquefaction

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ABSTRACT

Sargassum tenerrimum has been used for the production of bio-oil by hydrothermal liquefaction in water sub-critical conditions at a temperature range of 260–300 °C for reaction time 15 min. Maximum bio-oil (16.3 wt%) was obtained at 280 °C and maximum conversion was observed (75.8 wt%) at 300 °C. The solid residue yields decreased continuously from 61.2 wt% to 24.2 wt% as the temperature increased from 260 to 300 °C. The liquid products obtained upon hydrothermal liquefaction were characterized with the help of ¹H NMR, GC–MS and FT-IR techniques and bio-residue using FT-IR and XRD. Analysis of bio-oil showed that their components and functional structure of bio-oils were greatly distinguished and consisted of many compounds including phenols, ketones, aldehydes, acid, esters, alcohols, nitrogen-containing compounds, and hydrocarbons. From the GC–MS analysis it has been seen that, organic acid content in the bio-oils were decreased with the increasing temperature from 260 to 300 °C. The band at 1083 cm⁻¹ only appeared in the absorption profile of *S. tenerrimum* feed, which could be C-O connected with hydroxyl groups and were dehydrated after liquefaction. All the bio-oils showed higher percentages of aliphatic protons in the spectral region from 0.5 to 3.0 ppm. The analysis of bio-residue obtained at various temperatures showed typical amorphous nature that indicated richness of carbon content in the residue.

1. Introduction

Energy plays a crucial role in the economic growth and development of modern industrial society. Nevertheless, energy crisis and environmental concerns have become increasingly serious due to utilization of the limited fossil fuel [1]. To ensure energy safety and to reduce environmental problems, accelerating the development and utilization of clean and renewable energy sources has gained increasing attention over the past decades [2]. Biomass has been recognized as a renewable energy source that can be used to replace fossil fuels and absorb CO₂ from the atmosphere, reducing the greenhouse effect [3].

Biomass is currently regarded as the fourth largest primary energy source in the world, followed by coal, petroleum and natural gas [4]. As an energy source, it has been considered a potential substitute for fossil fuels because of its abundant capital, large distribution and being carbon neutral. Biomass can be classified basically into first, second and third generation categories according to the difference in raw materials obtained from the different sources [5]. Generally, first and second

generation biomass is produced from food crops such as corn, cassava and soybean and non-food crops such as rape straw, pine sawdust, etc. [6]. While these have a competition with food crops and land resources, the third generation aquatic biomass shows attractive promise by saving arable lands and stabilizing effective food supplies. Aquatic biomass is one of the most abundant sources of renewable energy and will be an important part of a more sustainable future energy system [7].

For producing biofuels from biomass, thermochemical methods such as gasification, pyrolysis and hydrothermal liquefaction (HTL) have been employed, of which hydrothermal liquefaction most commonly is used for wet biomass [8]. Hydrothermal liquefaction is a potential conversion route for biomass with high water content into bio-oil and produces liquid bio-crude through treatment of biomass at high pressures of 50–200 atm and temperatures of 250–400 °C [9]. This method exploits the properties of superheated fluids to reduce mass transfer resistances [10]. The high pressure also enables higher penetration of solvent into the biomass structure to facilitate fragmentation

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of biomass molecules [11]. The nature of the process allows for feedstock with high moisture content and therefore a wide range of material can be subjected to HTL to produce bio-crude. It is therefore the most promising technique for producing biofuels from wet biomass, having a lower reaction temperature and higher energy efficiency than the pyrolysis process since energy-intensive drying and dewatering steps are not imperative.

In the HTL procedure, water simultaneously acts as reactant and catalyst, making the process significantly different from pyrolysis. At conditions close to the critical point, water has several very interesting properties such as low viscosity and high solubility of organic substances, which make subcritical water an excellent medium for fast, homogeneous and efficient reactions [12,13,5]. Subcritical water behaves very differently from supercritical water. The dielectric constant decreases from 78 Fm^{-1} at 25°C and 0.1 MPa to 14.07 Fm^{-1} at 350°C and 20 MPa [14]. This gives rise to increased solubility of hydrophobic organic compounds such as free fatty acids [15]. The ionic product of water (K_w) is relatively high in the subcritical range (10^{-12} , compared to 10^{-14} at ambient conditions). The high levels of H^+ and OH^- under subcritical conditions mean that many acid or base catalyzed reactions such as biomass hydrolysis are accelerated [16]. Furthermore, the density of subcritical water falls in the range between those of ambient and supercritical conditions. Despite the high-temperature, the compressibility is still rather low. The relatively high density combined with the high dissociation constant of subcritical water favors ionic reactions [5].

Many researchers have been focusing on bio-oil production from aquatic biomass algae via the HTL process [8,17–25]. Shaobo et al., were investigated the production of crude bio-oils from three laboratory cultivated and two commercial grade algal biomass sources via hydrothermal liquefaction (HTL) process [21]. The HTL reaction was carried out at temperature ranging from 260°C to 340°C and residence time 10–40 min. The bio-oil yields were between 28 and 41%. The highest yield of 41.2% was obtained at 300°C with 20 min. residence time. The generated crude bio-oils have similar qualities as compared to those derived from commercial algae. The bio-oils were composed mainly of aliphatic compounds (fatty acids, alkanes) which can be readily upgraded and refined into value added transportation fuels (e.g., renewable diesel). Barreiro et al., were liquefied as raw biomass (RA), after extracting lipids (LEA) and after extracting proteins (PEA) in micro-autoclave experiments at different temperatures (300 – 375°C) for 5 and 15 min [22]. The results indicate that extracting the proteins from the microalgae prior to HTL may be interesting to improve the economics of the process while at the same time reducing the nitrogen content of the bio-crude oil. A complete set of experiments was carried out at a reaction time of 15 min for RA, LEA and PEA, varying the reaction temperature from 300 to 375°C . They showed the product yields after HTL for each feedstock and temperature used, as well as the elemental composition and high heating value of the bio-crude oil produced. Most of the organic mass from the feedstock was converted into bio-crude oil, with yields varying from 51.2 ± 3.4 to $69.2 \pm 1.9 \text{ wt}\%$. Raikova et al. [23] were study to bridge the gaps between previous accounts of macroalgal HTL by carrying out a more comprehensive screen of a number of species from all three major macroalgae classes, and examining the correlations between biomass biochemical composition and HTL reactivity. HTL was used to process thirteen South West UK macroalgae species from all three major classes (Chlorophyceae, Heterokontophyceae and Rhodophyceae) to produce bio-crude oil, a bio-char, gas and aqueous phase products. The reaction was carried out at temperature 345°C . The highest overall bio-crude yields were obtained for the two macroalgae of the genus *Ulva* (28.8% and 29.9% for *U. intestinalis* and *U. lactuca*, respectively), although the third Chlorophyta *R. riparium* performed significantly worse, yielding a modest 15.0% bio-crude product. *L. digitata* and *L. hyperboreana* yielded 16.4% and 9.8% bio-crude. Parsa et al., were carried out hydrothermal liquefaction of *Gracilaria gracilis* (*G. gracilis*) and *Cladophora glomerata*

(*C. glomerata*) macro-algae species harvested from Caspian Sea for bio-crude oil production at temperature 350°C and 15 min [24]. The bio-crude yield for *G. gracilis* and *C. glomerata* was 15.7 and 16.9 wt%, respectively with higher heating value (HHV) of 36.01 and 33.06 MJ/kg. Shakya et al., were performed a Hydrothermal liquefaction (HTL) of nine algae species at two reaction temperatures (280 and 320°C) to compare the effect of their biomass composition on product yields and properties [25]. Results obtained after HTL indicate large variations in terms of bio-oil yields and its properties. The maximum bio-oil yield (66 wt%) was obtained at 320°C with a high lipid containing algae *Nannochloropsis*. The higher heating value of bio-oils ranged from 31 to 36 MJ/kg and around 50% of the bio-oils was in the vacuum gas oil range while high lipid containing algae *Nannochloropsis* contained a significant portion (33–42%) in the diesel range. A predictive relationship between bio-oil yields and biochemical compositions was developed and showed a broad agreement between predictive and experimental yields. Through these studies, it was found that both the yield and the quality of bio-oil resulting from the HTL process were highly associated with the operating parameters such as reaction temperature, retention time, ratio of feedstock and solvent. HTL is more suitable for feedstock with high moisture content (e.g., algae), due to its inherent advantage of being a wet processing technique without the requirement drying the feedstock [3]. Furthermore, oil products produced from HTL have much lower oxygen content and moisture as compared to that after pyrolysis.

Aquatic biomass hydrothermal liquefaction is one of the options existing to meet the escalating energy demand and saving arable lands as well as to fight against the growing pollution loads on environment. In the present investigation, brown macroalgal biomass (*Sargassum tenerrimum*) commonly found in the seas of peninsular India is being examined under hydrothermal conditions. The hydrothermal liquefaction of waste aquatic biomass has been explored to understand the products profile at different temperature for utilization of whole biomass to produce fuel/chemicals. Effects of the reaction temperature (varied from 260°C to 300°C) with reaction holding time 15 min and water/feedstock mass ratio 1:6 were studied. The liquid products obtained upon hydrothermal liquefaction were characterized with the help of ^1H NMR, GC-MS and FT-IR techniques and bio-residue using FT-IR and XRD.

2. Material and methods

Sargassum tenerrimum (*ST*) (brown alga, phaeophyta family, Macroalgae) was sampled during the post-monsoon season from the intertidal region at Anjuna in north Goa. The collected samples were washed thoroughly with tap water followed by distilled water. They were first dried at room temperature by frequent turning over and then quick dried in an oven at 50°C for 2–3 h. The dried samples were coarsely crushed and powdered using an electric mixer-grinder.

2.1. Hydrothermal liquefaction

The HTL experiments were conducted in a 100 ml high pressure autoclave (Parr reactor) made of hastelloy at different reaction conditions of temperature. In a typical experiment, the reactor was loaded with *S. tenerrimum* with water as solvent (1:6 by weight). The reactor was then purged five times with nitrogen to remove the air inside. Reactants were agitated using a stirrer ($\sim 200 \text{ rpm}$). The reaction temperature was then raised to the desired value and maintained for 15 min. The pressure during the process was autogenous and maximum pressure was in the range of 40–83 bar under different reaction conditions. After the reaction, the reactor was left to cool down to room temperature to remove the reaction products. The gaseous products were vented and the liquid portion separated from solid residue using diethyl ether and vacuum filtration. The liquid portion was then extracted with an equal quantity of diethyl ether. The ethereal solution

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