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Hydrothermal liquefaction of macro algae: Effect of feedstock composition

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HIGHLIGHTS

- Hydrothermal liquefaction of three macro algae samples was performed.
- Compositional variations of macro algae were reflected in bio-oil & bio-residue yields.
- Maximum conversion and bio-oil (81% and 12%) was observed with macro algae UF.
- High percentage of aliphatic functional groups was observed in all bio-oils.

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ABSTRACT

Due to the increasing thrust on third generation biofuels, algal research has gained a lot of importance in the recent years. Effective utilization of algal biomass in a single step is necessary as it can produce fungible hydrocarbons in addition to a variety of valuable products.

Hydrothermal liquefaction does not require the energy intensive drying steps and is an attractive approach for the conversion of algae which has high moisture content. The objective of this study is to understand the effect of compositional changes of macro algae samples *Ulva fasciata* (MA'UF), *Enteromorpha* sp. (MA'E) and *Sargassum tenerrimum* (MA'ST) on product distribution and nature of products. Various macro algae samples were converted to bio-oil by hydrothermal liquefaction in a batch reactor at 280 °C for 15 min with biomass:water ratio of 1:6. The liquefaction products were separated into ether soluble fraction (bio-oil1), water-soluble fraction, solid residue and gaseous fraction. Maximum conversion of 81% was observed with macro algae (MA) UF. The effect of varying feedstock compositions were reflected in the bio-oil and bio-residue yields. The maximum conversion and bio-oil yield was observed with MA'UF due to the presence of higher carbohydrate content than other feeds. FTIR and NMR spectra showed high percentage of aliphatic functional groups for all bio-oils.

1. Introduction

It is now widely accepted that the end of cheap fossil oil era is already here and that the prices of crude oil will further increase in the years to come. This along with the desire to control the greenhouse gases urges the society to develop alternate sources for energy carriers and materials [1]. Biomass is seen to be an environmentally safe and economically feasible alternative to fossil fuels. It is necessary to derive the next generation liquid biofuels from biomass which do not compete with food supplies. Second generation biofuels are produced from lignocellulosic biomass while micro and macro-algae are used to produce third generation biofuels and chemicals. The use of macro algae for energy production has received less attention so far though macro algae have been cultivated since long for various purposes. The productivity is in the range of 1–15 kg m^{-2} y^{-1} dry weight (10–150 t_{dw} ha^{-1} y^{-1}) for a 7–8 month culture [2].

Hydrothermal technologies are broadly defined as chemical and physical transformations in high-temperature (200–600 °C), high-pressure (5–40 MPa) liquid or subcritical water which can be used for conversion of broad range of biomass feedstocks like agricultural, forest biomass residues, microalgae and macro algae [3]. Hydrothermal liquefaction generally produces bio-oil that is not miscible with water, has lower oxygen content and hence higher energy content than pyrolysis-derived oils [4] with high calorific values. It also produces a range of chemicals including vanillin, phenols, aldehydes, organic acids, etc. [5,6].

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Many efforts have been dedicated toward production of biofuels from microalgae [7] however fewer efforts have been reported about macro algae. Similar to microalgae, macro algae have a strong photosynthetic capacity and high growth rate. The marine macro algae *Enteromorpha prolifera* contains plenty of polysaccharides, proteins and a low content of fat and cellulose. It also has some essential mineral elements for human health and is mainly used as food or for medical purposes [8]. Aresta et al. produced biodiesel from green macro algae *Chaetomorphalinum* by comparison of two techniques: supercritical carbon dioxide (sc-CO_2) and thermochemical liquefaction at 250–395 °C and the results indicated that thermochemical liquefaction was more efficient although the yield was low [9]. Ross et al. classified macro algae as a good source of fuel by investigating the combustion and flash pyrolysis behaviors of five macro algae from the British Isles and analyzing the pyrolysis products [10]. Anastasakis and Ross [11] studied the influence of reactor loading, residence time, temperature and catalyst (KOH) loading on hydrothermal liquefaction of brown macro algae *Laminaria saccharina*. Maximum bio-crude yield obtained was 19.3 wt.%. Zhou et al. [12] studied the hydrothermal liquefaction of macro algae *E. prolifera* at temperatures of 220–320 °C. Highest bio-oil yield obtained was 23 wt.% at 300 °C with 5 wt.% Na_2CO_3. The bio-oil was seen to be composed of ketones, aldehydes, phenols, alkenes, fatty acids, esters, aromatics and nitrogen containing heterocyclic compounds.

In this study, the hydrothermal liquefaction of three different macro algae samples *Ulva fasciata* (MA'UF), *Enteromorpha* sp. (MA'E) and *Sargassum tenerrimum* (MA'ST) has been reported whose composition varies. The objective of this study was to understand the effect of composition of different macro algae samples on the bio-oil yield and product distribution. Liquid products were characterized with the help of FTIR, ^{1}H NMR and ^{13}C NMR and solid products using FTIR and SEM.

2. Materials and methods

2.1. Materials

The macro algae samples and compositional data (Table 1) were provided by CSIR-Central Salt & Marine Chemicals Research Institute (CSMCRI). MA'UF and MA'ST were collected from Veraval (N20°54.87′; E70°20.83′), Gujarat. MA'E was collected from Aryankundu (N9°17.717′; E79°16.212′), near Mandapam, Tamilnadu. The samples collected were first cleaned in seawater to remove sand and dirt particles from the thallus and then the wet material was brought to the laboratory where it was briefly rinsed in fresh water and then kept in shade and oven dried at 60 °C to constant weight. As seen from Table 1, all the macro algae have high carbohydrate content and lipid content was very low. The protein content was considerable in all the macro algae samples and showed high moisture and ash content [13,14].

2.2. Apparatus and experimental procedure

Hydrothermal liquefaction experiments were conducted in a 500 ml autoclave at 280 °C for 15 min using distilled water. In a typical hydrothermal liquefaction experiment, the reactor was loaded with 10 g of macro algae (wet basis) and 60 ml of distilled water. Then the reactor was purged five times with nitrogen to remove the inside air. Reactants were agitated vertically at ~50 cycles min^{-1} using stirrer. The temperature was then raised up to 280 °C at heating rate of 5 °C min^{-1} and kept for 15 min at 280 °C. After reaction, the reactor was left to cool down to the room temperature and gaseous products were vented. Solid and liquid products were separated by filtration under vacuum. The liquid portion was then extracted with equal quantity of diethyl ether. The etheral solution thus obtained was dried over anhydrous sodium sulfate, filtered and evaporated in a rotary evaporator at room temperature. Upon removal of diethyl ether, this fraction was weighed and designated as bio-oil1. After extraction, the remaining water phase contained the water-soluble hydrocarbons. Solid products were extracted with acetone in a Soxhlet extraction apparatus until the solvent in the thimble became colorless. After removal of the acetone under reduced pressure in a rotary evaporator, this fraction was weighed and designated as bio-oil2. Acetone insoluble fraction was dried at 80 °C then weighed, called as solid residue (bio-residue).

2.3. Analysis of feed and reaction products

The macro algae and the solid products obtained after the hydrothermal liquefaction of macro algae were analyzed by SEM and FTIR studies. The bio-oil samples were analyzed using FTIR and NMR. SEM images have been collected on FEI Quanta 200 F, using tungsten filament doped with lanthanum hexaboride (LaB_6) as an X-ray source, fitted with an ETD (Everhart Thornley Detector), which preferentially work as a secondary electron detector. The sample for SEM has been subjected to disperse on a carbon paper coated adhesive followed by gold coating. The ^{13}C NMR and ^{1}H NMR spectra of the bio-oil samples have been collected on Bruker Avance III 500 MHz NMR spectrometer using $CDCl_3$ as solvent. The FTIR spectra were recorded on Nicolet 8700 FTIR spectrometer.

3. Result and discussions

Hydrothermal liquefaction experiments of three macro algae samples were conducted in an autoclave at 280 °C for 15 min using distilled water. Reaction conditions have been selected based on our earlier studies and literature [15,16] to understand the effect of composition of different macro algae samples on the bio-oil yield and product distribution. The product distributions from hydrothermal liquefaction of various macro algae samples are presented in Table 2.

The varying feedstock compositions were reflected in the bio-oil yields calculated on dry basis. The total bio-oil yield was 7%, 12% and 9% for the three macro algae samples MA'E, MA'UF and MA'ST respectively. The maximum oil yield of 12% was obtained for the feed MA'UF and the total bio-oil yield was a minimum for MA'E with value of 7%. The total bio-oil was composed of the ether fraction (bio-oil1) obtained from extraction of liquid portion and the acetone fraction (bio-oil2) obtained from extraction of the solid fraction. The bio-oil2 has high viscosity and was seen to be a tarry liquid. MA'UF showed the maximum bio-oil1 (6%) and bio-oil2 (6%) yields. The yield of solid residue was 33%, 19% and 23% for MA'E, MA'UF and

Table 1
Compositional analysis of macro algae samples.

Species	Moisture (%)	Ash content (%)	Protein content (%)	Carbohydrate content (%)	Lipid content (%)
Ulva fasciata (MA'UF)	16.05	25.4 ± 0.1	14.30 ± 0.95	46.73 ± 2.25	1.83 ± 0.21
Enteromorpha sp. (MA'E)	35.21	23.2 ± 0.2	7.9 ± 0.5	39.9 ± 2.3	5.6 ± 0.2
Sargassum tenerrimum (MA'ST)	13.18	32.0 ± 0.1	10.75 ± 0.75	30.30 ± 1.55	2.03 ± 0.3