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Hydrothermal microwave processing of microalgae as a pre-treatment and extraction technique for bio-fuels and bio-products

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HIGHLIGHTS

- Hydrothermal microwave processing (HMP) allows effective extraction of phytochemicals.
- Nutrients such as N and P are extracted into the process water.
- HMP results in higher lipid extraction yields.
- High salt containing microalgae absorb more microwave energy.
- HMP results in improved bio-crude quality following hydrothermal liquefaction.

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ABSTRACT

Microalgae are regarded as a promising source of lipids for bio-diesel production and bio-products. The current paper investigates the processing of microalgal slurries under controlled microwave irradiation. Microwave power was applied to reach temperatures of 80, 100, 120 and 140 °C at a constant residence time of 12 min. Microwave irradiation led to disruption of the algal cell walls which facilitated lipid extraction. The influence of inorganic material on microwave heating was assessed for three strains including, *Nannochloropsis occulata*, *Chlorogloeopsis fritschii* and *Pseudochoricystis ellipsoidea*. Mass balances were calculated and showed that the amount of carbon, nitrogen and total mass recovered in the residue was highly dependent on process conditions and algae strain. Hydrothermal microwave processing (HMP) was found to be an effective pre-treatment for hydrothermal liquefaction and extraction of lipids and phytochemicals.

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1. Introduction

The development of third generation biofuels from microalgae has seen increasing interest in the last decade. Microalgae are able to fixate carbon dioxide from the atmosphere or from anthropogenic sources by photosynthesis more efficiently than terrestrial biomass due to their higher photosynthetic efficiency (Brennan and Owende, 2009). The high photosynthetic efficiency of microalgae and their ability to produce lipids has led to research investigating the production of bio-diesel by lipid extraction and transesterification to fatty acid methyl esters (FAME). FAMEs can be mixed with diesel and combusted in conventional diesel engines without the need for engine modifications. Even though there has been considerable amount of research into the production of bio-diesel from microalgae, only a few small pilot-scale projects are currently in operation. One of the main issues associated with large-scale production is the supply of sufficient high lipid algal biomass at a reasonable cost. Cultivation of high lipid strains is quite challenging as the strains can be sensitive to environmental influences and are not generally associated with the high growth rates which some high protein or mixed strains can achieve. Another issue with microalgae is the low concentration of biomass in water from cultivation with typical levels being a few g/L. This is a major concern when a dry feedstock is required in downstream processes, as required in many conventional lipid extraction techniques such as solvent extraction or bead milling. Recently hydrothermal processing of algae has been proposed and involves processing of a wet feedstock in hot compressed water. Depending on the severity of the reaction conditions, the process is classified as carbonization, liquefaction or gasification with the latter requiring higher temperatures and pressures. Hydrothermal processing does not require a high lipid feedstock as the protein and carbohydrate fraction of algae can also be converted to either a hydro-char, bio-crude or syngas. Hydrothermal processing of algae has significant potential in the manufacture of microalgae derived biofuels and has been recently reviewed (Biller and Ross, 2012).

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One unresolved challenge in hydrothermal processing is the extraction of phytochemicals prior to biofuel production. The extraction of value added compounds is essential to improve the economics of producing renewable fuels from microalgae and should be considered. Microalgae are a highly promising source of valuable phytochemicals such as pigments, recombinant proteins, mono- and polyunsaturated fats such as omega-3 fats and polysaccharides (Brennan et al., 2012). Limited studies have investigated the extraction of lipids and polysaccharides before further processing into biofuels. Miao et al. (2012) have recently investigated the sequential hydrothermal liquefaction of microalgae with extraction of valuable polysaccharides in the first step with subsequent bio-crude production of the residues (Chakraborty et al., 2012; Miao et al., 2012). Vardon et al. (2012) investigated the solvent extraction of lipids from *Scenedesmus* prior to hydrothermal liquefaction of the defatted microalgae (Vardon et al., 2012). Hydrothermal processing is a relatively severe procedure where close control of reaction conditions to achieve specific conversion to desired compounds can be quite difficult. Hydrothermal processing as a technique for the manufacture of chemicals is receiving increasing interest. For example the acid-catalyzed hydrothermal production of 5-(hydroxymethyl)-furfural and levulinic acid from cellulosic biomass has been recently proposed as a renewable source of platform chemicals (Potvin et al., 2011; Raspolli Galletti et al., 2012). Problems can arise however from induction heating, which may lead to unwanted side reactions at localized hot zones resulting in low extraction yields (Tsubaki et al., 2012). Microwave processing has been suggested to provide a more uniform method of heating as the heating occurs due to the rotation of dipolar molecules and vibrations of ions in solution in an electromagnetic field. This mode of heating can reduce residence times, increase reaction rates and provide more accurate control of reaction conditions (Tsubaki et al., 2012). Tsubaki et al. (2012) showed that the addition of halide salts within hydrothermal hydrolysis of cellobiose increases hydrolysis of carbohydrates resulting in a reduction of unwanted side reactions and energy consumption. It is therefore hypothesized that algae, which are naturally high in salts, could prove to be a promising feedstock for microwave processing. Microwave processing could either be used to facilitate extractions of valuable compounds such as polysaccharides or protein, as recently shown by Budarin et al. (2012) or applied as a means to produce a biofuel by microwave-mediated pyrolysis of algae (Budarin et al., 2011, 2012).

The current study aims to investigate the use of microwaves for the extraction of value added compounds before further processing to biofuels and bio-products. The influence of inorganic salts on hydrothermal microwave processing is investigated and the process is evaluated as a technique for extraction of valuable compounds as well as a pre-treatment for the production of biofuels via hydrothermal liquefaction. During direct hydrothermal liquefaction, proteins in microalgae are broken down and rearranged to complex nitrogen containing molecules which are found in the bio-crude (Biller and Ross, 2011). This produces a bio-crude with undesirably high nitrogen content which can lead to complications if the fuel is to be upgraded via hydro treatment/hydrogenation and increased NO_x emissions during direct combustion. It has previously been shown that proteins can be hydrolyzed to water soluble amino acids or extracted as proteins into the water phase during subcritical water treatment (Lamoolphak et al., 2006; Sereewatthanawut et al., 2008). If the proteins can be fractionated to the water phase during hydrothermal microwave processing it is expected that a bio-crude of lower nitrogen content can be produced by HTL. Du et al. (2012) performed work similar to this concept by subcritical water pre-treatment by conventional heating before flash pyrolysis to produce a bio-oil with fewer nitrogen containing compounds (Du et al., 2012).

2. Methods

Three microalgae strains were investigated; *Nannochloropsis occulata* was grown in-house at the University of Leeds. *Chlorogloeopsis fritschii* (*C. fritschii*) was grown by the Plymouth Marine Laboratory, UK. The *Pseudochoricystis ellipsoidea* strain (*P. ellipsoidea*) was isolated by the DENSO CORPORATION, Japan and has the unique ability to synthesize and accumulate aliphatic hydrocarbons (Imamura et al., 2012). All three strains were freeze-dried before use. Samples were prepared by mixing ~1 g of freeze-dried microalgae with 10 mL of deionized water to form a slurry. The low ash containing high-lipid fresh water strain was mixed with 0.1 M NaCl to investigate the effects of inorganic salt content on microwave processing. Samples of each strain were prepared in triplicate for each processing temperature used.

2.1. Microwave processing

Algal slurries were processed individually in a sealed quartz reaction vessel of 45 mL volume within a 1.2 kW Milestone StartSYNTH microwave oven (Milestone Srl, Italy). Samples were heated to 80, 100, 120 and 140 °C within 3 min, the temperature was then kept constant for 12 min before a fan was operated to cool the samples. Internal temperatures of the microalgal samples during processing were measured by an IR thermometer and logged on the control display. The energy used during microwave heating was determined through the integration of the power profiles using the computer's inbuilt $\int E/t$ function.

After the samples had been cooled, they were centrifuged for 15 min at 3500 rpm to separate the solid biomass sediment from the liquid phases to enable lipid extraction and compositional analysis. The liquid phase was then diluted to 250 mL with deionized water and analyzed for anions and cations using a DX-100 ion-chromatography analyzer (Dionex, USA). After centrifugation the solid samples were freeze-dried and analyzed for CHNSO content using a CE Instruments Flash EA 112 series elemental analyzer. Around 10 mg of sample was analyzed using a TA Instruments Q5000 thermo-gravimetrical analyzer; temperature was ramped to 105 °C in a constant flow of nitrogen to determine the moisture content and subsequently ramped at 10 °C/min to 900 °C and held for 15 min to obtain the pyrolysis devolatolisation profile. After 15 min, air was introduced to burn off the fixed carbon and determine the ash content of the biomass. Biochemical and metal analysis of the unprocessed biomass was performed as described previously (Biller and Ross, 2011; Ross et al., 2008). The solid residue was then coated with a thin gold layer before analysis by scanning electron microscopy (SEM) on a Zeiss EVO MA 15 (Carl Zeiss Microscopy, Germany).

2.2. Lipid extraction and analysis

Lipids were extracted from the microwaved samples and unprocessed algae by adding 25 mL of dichloromethane (DCM) to the dry biomass/residue and shaken continuously for 45 min in sealed sample containers. Subsequently, the DCM soluble fraction was separated from the defatted solids through a Whatman type 3 filter. Yields of lipids were determined gravimetrically after evaporation of the DCM at room temperature. Size exclusion chromatography of the lipids was carried out on a Perkin Elmer Series 200 HPLC instrument with a Varian PGel column of 30 cm length, 7.5 mm diameter, 3 μm particle size and a THF mobile phase flow rate of 0.8 mL/min. The lipids were additionally transesterified to FAME using methanol and sulfuric acid. Approximately 2 mL methanol was added to 200 mg of extracted lipids with one drop of sulfuric acid and agitated for 1 h at 55 °C in a shaking water bath. The FAME

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