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# Co-production of bio-oil and propylene through the hydrothermal liquefaction of polyhydroxybutyrate producing cyanobacteria

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## HIGHLIGHTS

- PHB breaks down into propylene and carbon dioxide under HTL conditions.
- The product distribution is not effected by other biomolecules present.
- PHB containing cyanobacteria (7.5%) yielded 2.6% propylene.
- Propylene could be co-produced with low-N bio-oils in a potential biorefinery.

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## ABSTRACT

A polyhydroxybutyrate (PHB) producing cyanobacteria was converted through hydrothermal liquefaction (HTL) into propylene and a bio-oil suitable for advanced biofuel production. HTL of model compounds demonstrated that in contrast to proteins and carbohydrates, no synergistic effects were detected when converting PHB in the presence of algae. Subsequently, *Synechocystis* cf. *salina*, which had accumulated 7.5 wt% PHB was converted via HTL (15% dry weight loading, 340 °C). The reaction gave an overall propylene yield of 2.6%, higher than that obtained from the model compounds, in addition to a bio-oil with a low nitrogen content of 4.6%. No propylene was recovered from the alternative non-PHB producing cyanobacterial strains screened, suggesting that PHB is the source of propylene. PHB producing microorganisms could therefore be used as a feedstock for a biorefinery to produce polypropylene and advanced biofuels, with the level of propylene being proportional to the accumulated amount of PHB.

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## 1. Introduction

Over the last 5 years, research on the direct hydrothermal liquefaction (HTL) of microalgae into fuel range compounds has gained significant momentum (Jazrawi et al., 2013; López Barreiro et al., 2013; Tian et al., 2014). Compared to the alternative process for the production of fuels from microalgae, the extraction of lipids followed by the transesterification into biodiesel, direct HTL offers a number of significant advantages: it is capable of converting the entire biomass fraction, not just lipids, and can therefore be used for the conversion of fast growing protein producing eukaryotic algae and cyanobacteria (hereafter collectively referred to as microalgae); it is conducted in the presence of high water loadings, and therefore only partial drying of the biomass is required; and it produces a wide variety of compounds which may be further upgraded into a range of fuels and chemicals (Lopez Barreiro et al., 2014; Tian et al., 2014). Despite this, a number of challenges remain: most notably, the upgrading of the resulting crude oils (which cannot be treated in conventional refineries due to their high nitrogen contents) and the utilisation of additional product streams to help subsidise fuel costs (Biller et al., 2013; Chuck et al., 2015).

Previous studies have investigated the relationship between bio-oil yields and the biochemical make-up of the algae (Li et al., 2014; Vardon et al., 2011). The three most important biochemical constituents of microalgae are proteins, lipids and carbohydrates, and their relative compositions depend both on the individual species and the selected growth conditions. These studies identified a strong relationship between lipid content and bio-oil yields, with lipid-rich algae producing the highest bio-crude yields. Using data

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from the conversion of model compounds and various microalgae species, Biller et al. estimated that the bio-crude yields from the different biochemical fractions range from 55% to 80% for lipids, 11% to 18% for proteins and 6% to 15% for carbohydrates (Biller and Ross, 2011). Similar yields were obtained by Teri et al. for pure model compounds, however, when converting mixtures of polysaccharides and proteins, enhanced oil yields were obtained at a reaction temperature of 350 °C (Teri et al., 2014). The authors suggested that this could be the result of Maillard reactions between sugars and amino acids formed from the carbohydrate and protein fractions respectively. Yang et al. experienced a similar behaviour using algae extracted crude polysaccharides and crude proteins (Yang et al., 2015). Yields obtained during the co-liquefaction of both compounds were enhanced compared to the yields of single compound liquefaction, also resulting in the highest energy recovery.

Besides these three main classes of biochemical compounds, some species of microalgae have been found to accumulate significant quantities of other types of compounds, such as algaenans, a series of acid and base-resistant aliphatic biomacromolecules (Versteegh and Blokker, 2004). During the HTL of these species, algaenans and algaenan derivatives were almost fully extracted into the biocrude phase at temperatures exceeding 300 °C, and can therefore help to increase potential yields of a low-nitrogen fuel precursor (Torri et al., 2012).

Some cyanobacteria (prokaryotic microalgae) also accumulate polyhydroxyalkanoates (PHAs), such as polyhydroxybutyrate (PHB), particularly in the presence of excess carbon and under nutrient (nitrogen, phosphorus) limited conditions (Markou and Nerantzis, 2013). The PHA content in the biomass can range from below 1% to over 50% and depends on the strain, the carbon and nutrient source and composition as well as on the cultivation conditions (Drosg et al., 2015; Panda et al., 2006; Wu et al., 2002, 2001). Fast growing thermophilic cyanobacteria such as *Chlorogloeopsis fritschii* PCC 6912 and *Synechococcus* sp. MA19 have been shown to accumulate PHB in excess of 6% w/w (dry weight) when grown at 50 °C (Hai et al., 2001).

PHAs are seen as a promising class of bio-polymers as they have equivalent properties to many currently available petroleum-derived plastics, with the added benefit of being biodegradable (Somleva et al., 2013). Despite this, PHA concentrations in fast-growing microalgae are usually too low to enable economic extraction. HTL could therefore represent a more effective method for utilising these compounds.

In this paper we investigate the potential of biopolymer-containing species of microalgae for conversion by HTL. To this end, models representing the four classes of biochemical compounds present in these species (lipids, proteins, carbohydrates and PHAs) were first converted in isolation and their product distribution determined. The results from the conversion of the model compounds were then compared to the yields obtained from the most extensively cultured and readily available cyanobacteria *Spirulina*, before liquefying *Spirulina* in the presence of varying concentrations of PHB (to compensate for its lack of natural PHB production, as a proxy for other potential cyanobacterial based PHB production platforms) to investigate if there is any interaction between the algal and the biopolymer compounds. Finally, three different species of cyanobacteria, both PHB and non-PHB producing, were liquefied and their product distribution analysed.

## 2. Methods

### 2.1. Materials

General lab solvents were purchased from Sigma–Aldrich and used without further purification. Deuterated chloroform ($CDCl_3$) for $^1H$ NMR analysis was purchased from Fluorochem. Rapeseed oil (*Co-operative Vegetable Oil*) was purchased from the Co-operative Food Supermarket, UK and contained 62% mono-unsaturates, 30% polyunsaturates and 8% saturated esters.

Dried Spirulina powder (*Organic Spirulina powder*) and protein (*soy protein isolate 90*) were purchased from Bulk Powders, Sports Supplements Ltd., UK. Corn flour (*Corn Flour by Sainsbury*) was obtained from Sainsbury's Supermarket Ltd., UK. Values for their biochemical composition were obtained from their packaging information. Polyhydroxybutyrate biopolymer granules were purchased from Goodfellow Cambridge Ltd.

### 2.2. Cultivation of microalgae

Stock cultures of *Anabaena* sp. (CCAP 1403/4A), *Synechococcus* sp. (WH7803) and *Synechocystis* cf. *salina* Wislouch (CCALA 192) were maintained under batch culture conditions and sub-cultured on a weekly basis. *Anabaena* cultures were maintained in BG11 media in 10 L bubble columns under 100 μmol photons $m^2\,s^{-1}$ irradiance on a 16 h:8 h light: dark cycle at 20 °C (±1 °C), according to literature precedent (Stanier et al., 1971).

*Synechococcus* sp. was grown in a saline version of BG11 (3.5% sea salt). Shear stresses prevented the growth of *Synechococcus* sp. in bubble columns and as such were grown in multiple 500 mL batches under the same irradiance measures and cycles and aerated by manual daily shaking. Strains were grown to mid log phase, and then sub cultured into either fresh medium, or medium lacking the nitrogen component ($NaNO_3$). Culture density was monitored spectrophotometrically.

*Synechocystis* cf. *salina* Wislouch (CCALA 192) – from the culture collection of autotrophic organisms – was cultivated in nutrient limited (nitrogen and phosphorous) mineral medium based on BG11 (Rippka et al., 1979) in a tubular photobioreactor with a working volume of 200 L for 21 days. The biomass was harvested with a nozzle separator (GEA Westfalia, Typ NA 7-06-067/-576) (disc outer diameter 162 mm), stored at −20 °C and lyophilised.

As the quantities of the individual samples were insufficient for separate HTL analysis, harvested *Synechococcus* and *Anabaena* biomass was combined into one sample grown under normal growth conditions (*Synechococcus* to *Anabaena* ratio of 3.53:1), and one grown under nitrogen starved conditions (*Synechococcus* to *Anabaena* ratio of 5.38:1), which will be referred to as *Synechococcus*/*Anabaena* and *Synechococcus*/*Anabaena-N*, respectively.

### 2.3. Biomass characterisation

The CHN content of all feedstocks (except PHB) was determined on a Carlo Erba Flash 2000 elemental analyser. The ash and moisture contents were determined by thermogravimetric analysis (TGA), under air flow, ramp rate of 10 °C $min^{-1}$ to 500 °C and 20 °C $min^{-1}$ to 900 °C.

Sugar (carbohydrate) content was determined according to literature precedent (Rao and Pattabiraman, 1989). Briefly, 3 mL conc. sulphuric acid is added to 1 mL algae sample (1 mg rehydrated in distilled water) ($n = 5$) and the reaction allowed to reach maximum temperature for 5 min before cooling to 25 °C. 1 mL 5% (w/v) phenol solution was added and the tubes stood at 25 °C for 30 min. The absorbance at $\lambda = 480$ nm was determined and glucose was used for standard curve.

Protein content was determined according to the biuret method (Bellou and Aggelis, 2012). Briefly, 1 mL culture (up to 8 mg dried algae rehydrated in distilled water) ($n = 5$) added to 0.75 mL $KH_2PO4$, (0.067 M pH4.5) and 3 mL NaOH (20% w/v) and incubated for 5 min. Thereafter 0.125 mL $CuSO_4{\cdot}5H_2O$ solution (25% w/v) was added and samples periodically shaken for 10 min then centrifuged. The absorbance at $\lambda = 540$ nm of the supernatant

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