



Contents lists available at ScienceDirect

Algal Research

journal homepage: www.elsevier.com/locate/algal

Phosphorus and nitrogen recycle following algal bio-crude production via continuous hydrothermal liquefaction

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ARTICLE INFO

Keywords:

Algae biofuel
Nutrient
Resource assessment
Maximum specific growth rates
Sustainability
HTL

ABSTRACT

Phosphorus and nitrogen are essential components of microalgal growth media. Critical to a wide range of biochemical processes, they commonly limit primary productivity. Recycling elemental phosphorus and fixed nitrogen after fuel conversion via hydrothermal liquefaction (HTL) of algae biomass reduces the need for mined phosphorus and synthetic nitrogen resources. *Scenedesmus obliquus* DOE 0152.Z and *Chlorella sorokiniana* DOE1412 were used as test organisms in assessing nutrient recycle of phosphorus from filtered solids collected downstream of the HTL reactor and nitrogen collected from the aqueous phase after gravimetric biocrude separation. Maximum specific growth rates were measured in growth media using HTL waste as the sole source of either phosphorus or nitrogen and were compared to an algal growth medium control (BG-11). The maximum specific growth rate of both organisms in the recycled phosphorus medium were nearly identical to rates observed in the control medium. Both organisms showed significantly reduced growth rates in the recycled nitrogen medium. *C. sorokiniana* DOE1412 adapted after several days of exposure whereas *S. obliquus* DOE0152.Z exhibited poor adaptability to the recycled nitrogen medium. After adaptation, growth rates observed with *C. sorokiniana* DOE1412 in the recycled nitrogen medium were $3.02 (\pm 0.13) \text{ day}^{-1}$, 89% of the control medium (3.40 ± 0.21). We further tested maximum specific growth rates of *C. sorokiniana* DOE1412 in a medium derived entirely from HTL byproducts, completely replacing all components including nitrogen and phosphorus. In this medium we observed rates of $2.70 \pm 0.05 \text{ day}^{-1}$, 79% of the control. Adding trace metals to this recycled medium improved growth rates significantly to 3.10 ± 0.10 , 91% of the control, indicating a critical element is lost in the conversion process. Recycling elemental resources such as phosphorus and nitrogen from the HTL biofuel conversion process can provide a significant reduction in media cost and improves the prospects for industrial scale, algae-based biofuels.

1. Introduction

Nutrient recycle in large-scale biofuel production scenarios is essential to both cost-effective and sustainable cultivation of biomass. Without nutrient recycling, biofuels will inevitably compete with food and feed crops for limited agricultural resources to meet the biological demands for key elements (N, P, Fe, etc.). Increasing concerns over the sustainability of mined phosphorus, for both conventional agriculture and biomass production, is a considerable barrier in large-scale algal cultivation for renewable petroleum replacements. While nitrogen is abundant and readily fixed from the atmosphere via the Haber-Bosch process, its synthesis is dependent on natural gas and therefore is a significant cost and energy burden for large scale agriculture. Although photosynthetic algae have a significant potential to provide a renewable fuel feedstock through utilization of non-potable water and non-

arable lands, current cultivation techniques have high nutrient demands. Recent analyses estimated that meeting 5% of the U.S. transportation fuel demand with microalgae would consume up to 50% of the 2011 U.S. agricultural consumption of phosphorus [1]. Further, even at the scale needed to meet approximately one quarter of the advanced biofuels 2022 goal of 21 billion gallons, established by the 2007 Energy Independence and Security Act (EISA) [2], current cultivation techniques would require 32–49% of the 2013 world surplus of phosphorus and 41–56% of 2013 world surplus of nitrogen fertilizers [3]. This relatively limited scale of production would only offset ca. 3.4% of total U.S. gasoline consumption [4], but would consume between 32 and 56% of the world's fertilizer stocks. It is therefore clear that increasing algal biofuel production to a scale that can replace liquid petroleum fuels would cause a direct impact to the global fertilizer market, which could in turn influence global prices for essential

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<http://dx.doi.org/10.1016/j.algal.2017.07.016>

Received 2 March 2017; Received in revised form 29 June 2017; Accepted 14 July 2017

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agricultural commodities (foods, feeds, fibers, etc.). Municipal wastewaters may offset a fraction of nutrient demand, but are not sufficient for current fuel consumption and productivity scenarios without nutrient recycling [5]. Furthermore, co-location of algal ponds with wastewater treatment facilities remains a logistical constraint. Therefore, regardless of production scheme or nutrient source, nutrient recycle is essential for large-scale, cost-effective biofuel production from algae biomass.

Hydrothermal liquefaction is a promising wet conversion technique for algal biomass, which facilitates the recycling of nutrients extracted from the biomass during the thermal conversion process back into the cultivation media. A number of recent studies have focused on the feasibility of recycling the nitrogen and phosphorus originating from hydrothermal liquefaction aqueous phase wastewater (HTL-AP) of microalgae biomass for cultivating microalgae, thereby reducing the demand and cost for N and P fertilizers in traditional growth media [6–14]. To the best of our knowledge, there are no published reports on quantifying the maximum specific growth rates of algae on recycled phosphorus, nitrogen, or media composed entirely of recycled components after the hydrothermal liquefaction conversion of algal biomass. If successfully implemented, this method of fuel processing may alleviate much of the nutrient demand implications predicted in large-scale scenarios [3,5,15,16]. Additionally, precipitating solids within the HTL reactor reduces the formation of emulsion at the oil-water interface when gravimetrically separating the bio-crude and the nitrogen-rich aqueous phase [17].

The specific objectives of this study were to 1) determine if phosphorus from the solid precipitate recovered during hydrothermal processing of algal biomass supports microalgae growth similar to the chemical salt (K_2HPO_4) used in our laboratory algal growth medium (BG-11) and if an extraction step is needed to liberate the precipitated phosphorus and 2) determine if nitrogen recovered from the HTL-AP after gravimetric separation of the bio-crude supports microalgal growth. We report here complete replacement of the phosphorous and nitrogen media components for two well-characterized microalgae *Scenedesmus obliquus* DOE015.Z and *Chlorella sorokiniana* DOE1412.

2. Materials and methods

2.1. Continuous hydrothermal liquefaction

A continuous hydrothermal liquefaction reactor was used in the processing of microalgal biomass as previously described [18]. In brief, the algae feedstock (*Tetraselmis* sp. obtained from Cellana, Inc.) was prepared to ensure a relatively homogeneous paste of ca. 20% (w/v) solids (Fig. 1). The algal paste was pumped through the reactor under

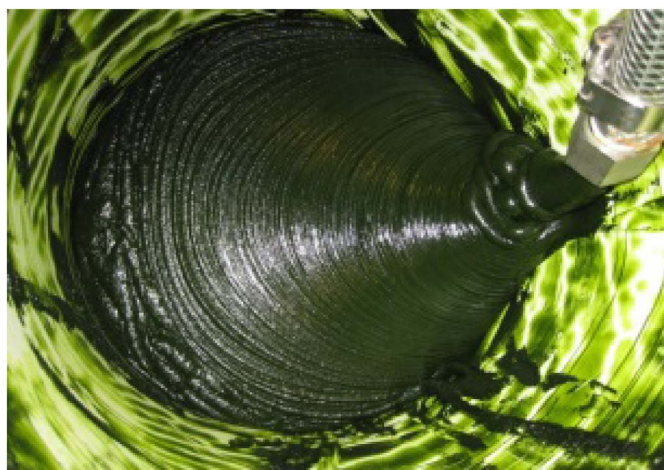


Fig. 1. Slurry of algal biomass feedstock (*Tetraselmis* sp.) at ca. 20% (w/v) solids.



Fig. 2. Precipitated solids, derived from algal biomass (*Tetraselmis* sp.), collected in the HTL reactor filter trap.

pressure using a modified Isco 500D dual syringe pump at an approximate liquid hourly space velocity (LHSV) of 2.1 L/L/h.

2.2. Phosphorus recovery and extraction

During the liquefaction of the algal biomass, precipitated mineral solids (Fig. 2) were recovered from the liquid stream. These precipitated solids were recovered at reaction temperature and pressure in an oil-jacketed filter trap and blow-down vessel, allowing a solid-free liquid phase to form as previously described. Precipitated solids obtained during the hydrothermal liquefaction runs were extracted in 0.25 M H_2SO_4 and stirred for 2 h. at room temp. Phosphorus was extracted at different acid concentrations for variable durations, under a range of temperatures. Phosphorus recoveries from filter solids generated by the HTL of *Tetraselmis* biomass were found to be effective at 20 °C with 0.25 M sulfuric acid at an acid to solids ratio of 20 mL/g for 120 min, increasing temperatures (to 75 °C) and acid concentrations (to 0.5 M) did not improve extraction results, whereas an acid concentration of 0.1 M provided incomplete extraction (Fig. 3).

2.3. Elemental compositional assessment

Neat and acid-extracted filter-solids were analyzed by inductively-coupled plasma- optical emission spectrometry (ICP-OES, Perkin Elmer, Optima 7300DV) (Fig. 4). Nitrogen content was measured as both total nitrogen via CHN analyzer following ASTM D5373/D5291 (Perkin Elmer 2400 II CHN Micro Analyzer) and ammonia-nitrogen using colorimetric determination (HACH TNT832).

2.4. Microalgae and cultivation conditions

The bioavailability of recovered phosphorus and nitrogen was tested by measuring maximum specific growth rates in cultures of *Scenedesmus obliquus* DOE015.Z and *Chlorella sorokiniana* DOE1412 obtained from Dr. Juergen Polle of the City University of New York [19]. The strains were cultivated in a modified BG-11 medium [20] with 17.6 mM NO_3^- , 0.66 mM PO_4^{3-} , due to elemental concentrations found in the filter solids (Fig. 4), Copper was omitted and Manganese was reduced by 50% from the standard BG-11 trace metals. The concentration of elemental phosphorus (MW = 30.97 g/mol) in the acid-extracted filter solids was 3515 mg/L, equivalent to 113.4 mM P. This P concentration is about 172 times higher than the concentration in the modified BG-11 medium that is used as a control medium (i.e., 0.66 mM P). Therefore, it was feasible to substitute the P at the required concentration from the HTL filter solids sulfuric acid digestate for the K_2HPO_4 currently used in the

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