



## Fate and reuse of nitrogen-containing organics from the hydrothermal conversion of algal biomass



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### A B S T R A C T

Hydrothermal (HT) conversion is a promising and suitable technology for the generation of biofuels from microalgae. Besides the fact that water is used as a “green” reactant and solvent and that no biomass drying is required, the technology offers a potential nutrient source for microalgae culture using an aqueous effluent very rich in essential inorganic nutrients. However, upon continuous and multiple recycling of this HT effluent, the recalcitrant organic fraction is likely to increase and may potentially attain toxic thresholds for microalgae use. In this work, we show the presence of recalcitrant N-containing organic compounds (NOC's) in the HT effluent. The most prominent NOC's in the extracts were carefully examined for their effect on microalgae, namely 2-pyrrolidinone and  $\beta$ -phenylethylamine ( $\beta$ -PEA). The first set of experiments consisted in testing these two substances at three different concentrations (10, 50 and 150 ppm) using three different microalgae strains: *Phaeodactylum tricoratum*, *Chlorella sorokiniana* and *Scenedesmus vacuolatus*. The confirmed half maximal inhibitory concentration (IC50) was approximately 75 ppm for all tested species. In the second set of experiments, *P. tricoratum* was grown using diluted HT effluent. Experimental conditions were set by adjusting the nitrogen concentration in the HT effluent to be equal to a known commercial medium. The concentrations of specific NOC's were lowered to concentrations of 8.5 mg/L 2-pyrrolidinone and 0.5 mg/L  $\beta$ -PEA after dilution. The growth of *P. tricoratum* using the diluted HT solution was kept constant with no evidence of inhibition or consumption of NOC's, as the concentration of the specific compounds remains the same before and after growth. Therefore, in order to avoid effects of accumulation of NOC's upon continuous recycling, the HT effluent was pumped through the existing hydrothermal gasification unit as a water clean-up step. The conversion of NOC's to ammonium was successfully achieved.

### 1. Introduction

Although hydrothermal (HT) conversion technologies of algal biomass using supercritical water are able to provide an aqueous effluent very rich in essential inorganic nutrients [1], this highly efficient process may still result in some unprocessed organic recalcitrant traces. In our previous studies [1,2], we have demonstrated the feasibility of cultivating microalgae by hydrothermal processing of the effluent even if a small fraction of organic carbon and nitrogen remained in the

media. However, upon continuous and multiple recycling of this hydrothermal effluent, in principle suitable for algal growth, this recalcitrant organic fraction is likely to increase and potentially attain toxic thresholds [3].

The formation of recalcitrant organic products is mainly the result of algal biomass decomposition through a complex set of chemical reactions that occur during the hydrothermal gasification process [4]. Typically, large macromolecules (proteins, lipids and carbohydrates) are reduced to smaller ones via multiple reaction pathways such as

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depolymerization, thermolysis, hydrolysis and cross-reactions between degradation intermediates. Moreover, lighter molecules may also undergo secondary reactions, such as condensation and aromatization, leading to the formation of stable, less reactive and undesirable, products (e.g., melanoidins, benzenes, phenols, phenylethanones, and Maillard products) [5]. According to Brandenberger et al. [6], the consecutive products of carbohydrate and protein degradation led to the formation of radical scavengers, such as nitrogen containing cyclic organic compounds via Maillard reaction. The reaction of intermediates formed during hydrothermal biomass gasification with each other or with hydrogen produced, by the water gas shift reaction, has a significant influence on the process. The presence of these less reactive compounds leads to a decrease in both syngas formation and nitrogen recovery.

Removing these N-containing organics from different types of waste effluents into gas phase products has been most commonly addressed through thermochemical technologies, such as supercritical water oxidation (SCWO) [7]. For instance, the removal of an aromatic amine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), through SCWO was studied recently and confirmed the efficiency of this method as the compound was completely oxidized at 450 °C [8]. An alternative process to make use of these effluents is supercritical water gasification (SCWG). This process has the advantage of promoting energy recovery through a larger net reduction of total organic carbon. N-containing compounds could be converted to methane and the nitrogen released as ammonia, which may then be used as fertilizer. Chakinala et al. [9] focused on the screening for an efficient catalyst able to completely convert the organics contained in the aqueous fraction of hydrothermal liquids. They concluded that a ruthenium (Ru) catalyst proved to perform best in terms of gasification efficiency. Moreover, they suggested catalytic hydrogenation as a pre-treatment to convert the sugar monomers into “polyols” to avoid char and coke formation under certain conditions. Another study tried the gasification of indole in supercritical water but the almost complete conversion (98%) was attained only at temperatures above 600 °C together with a high yield of ammonia approaching the theoretical maximum. However, benzene resulted as a liquid-phase product and started to decompose only at temperatures above 700 °C [10]. That same study reached the conclusion that a catalyst was necessary to render the process feasible. Mansur et al. [11] have tried the hydrothermal decomposition of 2-pyrrolidinone into lighter components at 350 °C and atmospheric pressure, using  $ZrO_2-FeO_x$  as catalyst, where oxidation takes place using lattice oxygen on the catalyst. However, this resulted in the polymerization of this compound into heavy components. Finally, Elliot et al. [12] used catalytic hydrothermal gasification using a 7.8 wt% Ru catalyst on a partially graphitized carbon extrudate at 348 °C and 20 MPa (8 h) to gasify the soluble remaining organics in the HT effluent from the conversion of macroalgae, resulting in an almost complete gasification.

In the present study, a thorough characterization of the soluble recalcitrant organics in the HT effluents was investigated. Toxicity bioassays with the most critical substances were tested on three different microalgal species to determine the half maximal inhibitory concentration (IC50). The growth test performed with low nitrogen-containing organics NOC's content (diluted HT effluent) has revealed no significant consumption of these compounds which means that an increase of their concentration upon continuous recycling is expected. Therefore, in this work, we propose to gasify the soluble remaining organics in the HT effluent using the existing hydrothermal gasification unit when NOC's concentration reaches toxic thresholds. To the best of our knowledge, this is the first time that a water-cleaning step was applied to the hydrothermal effluent obtained from the conversion of microalgae biomass. No further algal growth test with the catalytically gasified effluent was included because in our previous study we have shown the ability of those species to cope with the diluted HT effluent, as long as the organic compounds are maintained at low levels [1].

## 2. Materials and methods

### 2.1. Hydrothermal liquefaction (HTL) and catalytic gasification (HTCG) experiments in the continuous reactor setup

The HT conversion plant consists of six main sections: feeding section, salt separator, salt removal section, gasification reactor, pressure control, and release phase separator. The latter was described in detail elsewhere [13]. Briefly, *P. tricornutum* biomass slurry was pumped at the desired flow rate to the salt separation unit (SITEC, stainless steel grade) using a hydraulic system. The salt separator has two outlets, one for delivering the liquefied feed to the gasification reactor (located at the top) and another for extracting the concentrated HT effluent (located at the bottom). The liquefied feed leaving the top of the salt separator was transferred to the catalytic reactor from the bottom (SITEC, stainless steel grade 1.4435; inner length, 1515 mm; inner diameter, 36 mm). The lower part of the reactor was filled with 713 g (on a wet basis, 5.2 wt%  $H_2O$ ) of a commercial ZnO adsorbent (Johnson Matthey Catalysts, KATALCO 32–5) containing 60–100 wt% of ZnO, and the upper part was filled with 493 g (on a dry basis) of a commercial 5% Ru/C catalyst (BASF). Separation of different products at the end of the experiment was carefully performed starting with release of gases into gas bags while the liquid HT effluents, namely salt brine (SB, obtained from the salt separation unit, is a very rich effluent containing both inorganic and organic compounds) and reactor water (RW, obtained from the gasification unit and containing a very small fraction of inorganics) were vacuum filtered. A simplified flow-chart is displayed in Fig. 1 and the summary of the process parameters of the HTCG provided in Table 1.

The elemental mass balance of HTL products was calculated based on the element recovery in the aqueous phase. Once we determined the element distribution for the aqueous phase, the rest is considered to have entered the oil phase. The element recovery (% w/w) calculation is based on the ratio of the weight fraction of a particular element in the HT aqueous phase to the weight fraction of the same element in the original feedstock.

#### 2.1.1. Chemical characterization of salt brine effluent (SB)

The SB was thoroughly characterized for its organic content. Total organic carbon (TOC) measurements were performed with a TOC analyzer (Elementar) and ultimate analysis (elemental carbon, nitrogen and sulfur) using a CNS analyzer (Vario EL cube). Total nitrogen content (TN) was additionally used to calculate the total content of proteinaceous nitrogen (PN) value, obtained by multiplication using a species-specific conventional factor (4.87) for *P. tricornutum* [14]. Oxidizable organics (COD) and phenols were additionally tracked through colorimetry test cuvettes (HACH®). The HT content in organic acids was also analyzed by High-performance liquid chromatography (Agilent Technologies, 1260 infinity) coupled to a refractive index detector (HPLC-RI) using a Biorad Aminex HPX-87H column at 60 °C. The injection volume was 20  $\mu$ L, using 0.005 M sulfuric acid as a mobile phase, and the flow rate was set at 0.6 mL/min. The RW effluent was only used to dilute the SB for the preparation of algae medium, as the former had a very low inorganic content and could be used as a water supply for dilution.

#### 2.1.2. Chemical characterization of cyclic amides found in the hydrothermal aqueous phase

We have followed a known method for the extraction of heteroaromatic compounds [15]. Specific NOC's were profiled using gas chromatograph coupled to a mass spectrometry (GC–MS) detector (Agilent Technologies, 7802A). The separation was achieved using a Varian CP-sil 8 column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m), using helium as a carrier gas at a flow rate of 1 mL/min. 1  $\mu$ L of the extract was injected at 275 °C. NOC's were at first identified using the library program (internal library, NIST 17) and then confirmed using mass spectra. The most

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