Bioresource Technology 247 (2018) 250–258

Contents lists available at ScienceDirect

Bioresource Technology

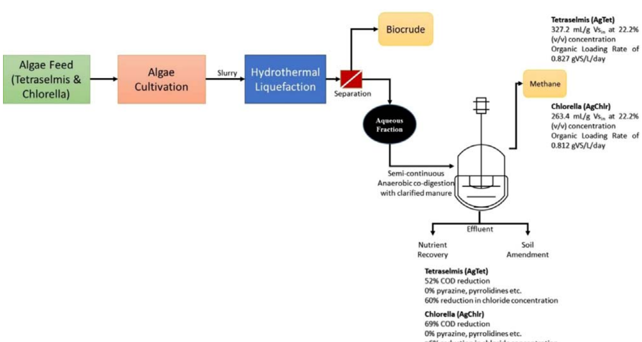
journal homepage: www.elsevier.com/locate/biortech

Anaerobic digestion of organic fraction from hydrothermal liquefied algae wastewater byproduct

Sebastian Fernandez[a], Keerthi Srinivas[a], Andrew J. Schmidt[d], Marie S. Swita[d], Birgitte K. Ahring[a,b,c,*]

[a] Bioproducts, Sciences and Engineering Laboratory, Washington State University, Tri-Cities, 2710, Crimson Way, Richland, WA 99354, USA
[b] Biological Systems Engineering, L.J. Smith Hall, Washington State University, Pullman, WA 99164, USA
[c] The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99163, USA
[d] Chemical and Biological Processes Development Group, Energy and Efficiency Division, Pacific Northwest National Laboratory, Richland, WA 99354, USA

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Anaerobic digestion
Chlorella
Hydrothermal liquefaction
Methane
Testraselmis
Wastewater treatment

ABSTRACT

The wastewater stream from hydrothermal liquefaction (HTL) process used in biofuel production, contains a large amounts of organic compounds where several can be regarded as environmentally hazardous and requires significant treatment before disposal. In this study, semi-continuous anaerobic digestion is used to degrade the organic fraction of wastewater streams from HTL of the algae Tetraselmis (AgTet) and Chlorella (AgChlr). Results indicated high methane yields at 20–30% (v/v) HTL wastewater together with clarified manure, producing 327.2 mL/gVS$_{in}$ (or volatile solids in feed) for AgTet and 263.4 mL/gVS$_{in}$ for AgChlr. There was a significant reduction in methane production at concentrations higher than 40% (v/v) HTL wastewater in the feed, possibly due to the accumulation of chloride salts or inhibitory compounds such as pyridines, piperidines and pyrrolidines. This was further confirmed by comparing COD, salt and the ammonia concentrations of the effluents after anaerobic digestion at different concentrations of wastewater in manure.

1. Introduction

Algae is an attractive form of biomass for production of sustainable biofuels, in part due to their high lipid content, ability to fix atmospheric and industrial carbon (in form of CO_2), high growth rates, ability to thrive in relative harsh environments. Algae cultivation does not compete with agricultural sources and several studies have shown that algae based biofuels can be used for drop-in replacements of

* Corresponding author at: Bioproducts, Sciences and Engineering Laboratory, Washington State University, Tri-Cities, 2710, Crimson Way, Richland, WA 99354, USA.
E-mail address: bka@wsu.edu (B.K. Ahring).

http://dx.doi.org/10.1016/j.biortech.2017.09.030
Received 15 July 2017; Received in revised form 31 August 2017; Accepted 1 September 2017
Available online 06 September 2017
0960-8524/

gasoline, diesel and jet fuels (Albrecht et al., 2016; Singh and Gu, 2010). There are, however, some disadvantages with an algal biorefinery especially related to location (algae needs lot of sunlight to grow) and dewatering (before conversion of algal biomass conversion to high-value products). Hydrothermal liquefaction (HTL) is a useful method, which can be used for conversion of algae biomass into biofuel production. It has the advantages that it can work on wet biomass, and, therefore, will not demand energy-consuming drying/dewatering processes for the algae biomass (Bridgwater et al., 1999). During hydrothermal liquefaction, the biomass is thermo-chemically converted to bio-crude, by applying heat (200–350 °C) and pressure (15–20 MPa). At these sub-critical and near-critical conditions, water acts as a reaction medium due to its low pH (King and Srinivas, 2015) and breaks down the biomass into smaller molecules, which can be further converted into bio-oil, char, water-soluble substances and gas. Recovered bio-oil can then be upgraded to fuels using different technologies as has been studied and optimized by Pacific Northwest National Laboratory (PNNL) with great success for the production of liquid biofuel product (Scott et al., 2010; Elliott et al., 2013). Due to the high water content in algal biomass, hydrothermal liquefaction generates liquid byproducts that contain several phenolic and aromatic compounds that require treatment before disposal of the final products. This is further needed before the nutrients and water can be recycled, which is of importance for the economics of algae biorefineries. Previous studies has shown that some of the organic compounds distributed into aqueous phase during HTL treatment of microalgae includes indoles, pyridines, pyrrolidinones, pyridinols, ketones, amides, alcohols, aromatic and carboxylic acids (Chen et al., 2017a). Studies have also indicated that almost 40% of carbon and 80% of nutrients from the feedstock is usually collected in the wastewater stream after HTL treatment (Yu et al., 2011).

Anaerobic digestion is a low-cost and low energy-intensive technique that uses naturally-available microorganisms to efficiently degrade the organic compounds present in a feed substrate (in absence of oxygen) to produce methane (Yen and Brune, 2007). Anaerobic digestion has been significantly studied for conversion of waste and wastewaters and there are many full-scale biogas plants all over the world. Apart from its intended purpose to degrade environmentally-harmful phenolics from HTL wastewater, it is hypothesized that anaerobic digestion is suitable for treatment of hydrothermal liquefied (HTL) wastewater since it can aid in recycling the nutrients that are necessary for algae growth and produce biogas, which can supply energy that can be substituted with existing energy sources for the algal biomass production and for the separation of water from the biofuel produced through HTL process (Harun et al., 2011; Park and Li, 2012; Zhao et al., 2014; Zhu, 2015). Anaerobic digestion has been previously used to detoxify wastewater stream from bioethanol production resulting in over 80% (w/w) COD removal and a high methane yield of 529 mL methane/g VS_{in} or volatile solids of feed/influent (Torry-Smith et al., 2003; Uellendahl and Ahring, 2010). Due to the extraction process used to recover the bio-oil (that uses organic solvents) and the high temperatures and pressures used upfront, HTL wastewater stream will contain inhibitory toxic compounds, in the form of aromatics and phenolics produced during the degradation of biomass, which can be inhibitory for cell growth and methanogenesis (Boyd et al., 1983). Cytotoxicity studies on the HTL wastewater stream from Spirulina showed high microbial inhibition by piperidones, amino phenols and pyridines contributing almost 30% of the total toxicity present in the HTL wastewater (Pham et al., 2013). Previous work has been done for reducing the effect of such inhibitory compounds present in HTL wastewater stream from algae feedstock by using activated carbon (Pham et al., 2013; Zhou et al., 2015). While the process (focused mainly on energy recovery) was capable of achieving higher net energy recovery efficiency when using activated carbon before the anaerobic digestion, the process was still found to be inhibited by the phenolic or aromatic compounds present in the wastewater stream when concentrations higher than 33.3% HTL wastewater was added to the feed. In the absence of activated carbon, the AD process was significantly inhibited even at concentrations as low as 13.3% HTL wastewater in feed. This study was, however, done using batch anaerobic digestion and the toxicity effect of the phenolic or aromatic compounds present in HTL wastewater can be significantly reduced using a continuous anaerobic digestion process allowing for gradual adaptation to the wastewater. Previous studies have shown significant lignin degradation in CSTR reactors through conversion of aromatics from manure material, which was wet exploded at high temperature/pressure with oxygen addition (Ahring et al., 2015). The primary goal of the present study is to examine the toxicity of inhibitory compounds on semi-continuous anaerobic digestion of the HTL wastewater and to optimize the conditions for maximum energy and nutrient recovery from the wastewater. The results from this study can have significant implications on the energy balance and techno-economics in algal biorefineries as well as provide a less toxic wastewater stream that can be used for soil amendment or algal growth or further co-digested with manure or sewage sludge to produce more methane.

2. Materials and methods

2.1. Feedstocks and materials

Two HTL algae byproduct samples (Testraselmis AGT = AGTet, and Chlorella AGC = AGChlr) were received from PNNL and kept in the refrigerator until further use. Table 1 shows the initial characteristics of the wastewater supplied by PNNL for the experiments.

Manure was obtained from Five D Farms in Pasco, WA and clarified through centrifugation at 10,000 rpm to remove any solids. The clarified manure was primarily used as a nutrient base (or feed) to ensure good growth of the anaerobic microflora instead of using water and expensive nutrients. The inoculum for the experiments was obtained from an existing laboratory digester operated with clarified manure as feedstock and was found to have the same composition as that of clarified manure shown in Table 1.

2.2. Experimental setup

The anaerobic digestion of the HTL wastewaters supplemented with clarified manure was done using Applikon® ezControl Autoclavable bioreactor (Applikon Biotechnology B.V, Netherlands). The process schematic of the semi-continuous anaerobic digestion system is shown in Fig. 1. As can be seen from Fig. 1, the clarified manure (feed) and the HTL wastewater are fed into the Applikon reactor using constant flow pumps connected to a timer. The flow rates in the pumps running HTL wastewater and clarified manure respectively were varied (~1% v/v increase in concentration per day) to obtain different concentrations of the HTL wastewater-feed mixture (0–80% v/v) in the digester and the digester is stirred continuously (200 rpm) to ensure homogeneity. Level rods are placed in the digester and the outlet from the digester flows into an effluent tank so that the reactor volume does not change during the operation. A constant volume of 1 L was maintained throughout the experiments. The stirring, effluent flow rate, reactor volume (set using

Table 1
Characteristics of Feed streams.

Feed stream	pH	COD mg/L	NH_4-Nmg/L (as N)	Chloride (ppm)	Sulphate (ppm)	Volatile Solids (wt %)
AgTet	8.60	87,300	4975	12,900	630	4.80
AgChlr	8.44	75,200	6500	203	610	4.11
Clarified Manure (feed)	7.23	4000	802	162	137	1.40